

**DOCTORAL (PhD) DISSERTATION**

**IMPROVING IN CORROSION, TRANSPORTATION AND  
STORAGE PROPERTIES OF REAL WASTE DERIVED  
PYROLYSIS OIL**

**Made in the framework at the  
University of Pannonia  
Doctoral School of Chemical Engineering and Materials Science**

DOI:10.18136/PE.2020.768

**Written by:**  
**Fekhar Bahmed**  
Mechanical engineer

**Supervisor:**  
**Norbert Miskolczi, PhD**  
M. eng. in Chemical Engineering  
Associate professor

**University of Pannonia**  
Faculty of Engineering  
Research Centre for Biochemical, Environmental and Chemical Engineering  
MOL Department of Hydrocarbon and Coal Processing

Veszprém  
2020

IMPROVING IN CORROSION, TRANSPORTATION AND  
STORAGE PROPERTIES OF REAL WASTE DERIVED  
PYROLYSIS OIL

Thesis for obtaining a Ph.D. degree in the Doctoral School of Chemical Engineering and  
Material Sciences of the University of Pannonia

In the branch of Bio-, Environmental-, and Chemical Engineering Sciences

Written by Fekhar Bahmed

Supervisor: Dr Norbert Miskolczi

Propose acceptance (yes / no) .....  
(supervisor)

As a reviewer, I propose acceptance of the thesis:

Name of Reviewer: ..... yes/no .....  
(reviewer)

Name of Reviewer: ..... yes/no .....  
(reviewer)

The PhD-candidate has achieved .....% at the public discussion.

Veszprém, .....  
Chairman of the Committee)

The grade of the Ph.D. Diploma ..... (..... %)

Veszprém, .....  
(Chairman of UDHC)

## LIST OF CONTENT

Introduction.....	1
1. LITERATURE SUMMARY .....	2
1.1. Resources, wastes, energy consumption and sustainability .....	2
1.2. The problems of waste polymers .....	5
1.2.1. Plastic .....	5
1.2.2. Biomass .....	6
1.2.3. Paper.....	8
1.2.4. Municipal Solid Waste.....	8
1.3. Processes for waste polymer utilization.....	9
1.3.1. Landfilling.....	9
1.3.2. Mechanical recycling .....	10
1.3.3. Chemical recycling by solvents .....	10
1.3.4. Thermal processes .....	10
1.4. Waste polymer pyrolysis for oil production.....	13
1.4.1. Materials.....	14
1.4.2. Co-pyrolysis .....	18
1.5. Pyrolysis reactor configurations.....	19
1.6. Product properties of the waste polymer pyrolysis .....	21
1.6.1. Gases .....	21
1.6.2. Pyrolysis oil.....	21
1.6.3. Char .....	23
1.7. Further utilization of pyrolysis oils .....	24
1.8. The problem of pyrolysis oil .....	25
1.9. Stability improving of the pyrolysis oil .....	27
1.9.1. Pre-situ quality improving.....	27
1.9.2. In-situ quality improving.....	28
1.9.3. Post-situ quality improving .....	29
1.9.4. Ex-situ quality improving .....	29
1.10. Tests for investigation of the long-term property of the pyrolysis oil .....	29
1.10.1. Aging tests.....	30
1.10.2. Corrosion tests.....	32
1.11. Main conclusion and critical evaluation of available literature .....	33
2. EXPERIMENTAL PART.....	35
2.1. Raw materials.....	35
2.1.1. Waste plastic, biomass and paper.....	35
2.1.2. Raw materials for comparative study of different aging tests.....	36
2.2. Catalysts .....	37
2.3. Processes for pyrolysis .....	39
2.3.1. Batch process .....	39
2.3.2. Continuous process .....	40
2.4. Analytical methods .....	40
2.4.1. Raw materials.....	40
2.4.2. Catalysts .....	41
2.4.3. Gases .....	41
2.4.4. Light oil.....	41
2.4.5. Aging tests.....	42
2.4.6. Corrosion tests.....	42
2.5. Research plan .....	43

3.	RESULTS AND DISCUSSION .....	46
3.1.	Analysis of raw material and catalysts .....	46
3.1.1.	Raw materials .....	46
3.1.2.	Catalysts .....	48
3.2.	Comparison of different aging methods .....	50
3.2.1.	Pyrolysis oils .....	51
3.2.2.	Density .....	52
3.2.3.	Viscosity .....	53
3.2.4.	Total Acid Number .....	55
3.2.5.	Solid deposition .....	56
3.2.6.	Main conclusions of the comparative study .....	58
3.3.	Pyrolysis of contaminated plastic waste .....	58
3.3.1.	Product yields .....	58
3.3.2.	Products properties .....	59
3.3.2.1.	<i>Gases</i> .....	59
3.3.2.2.	<i>Light oil</i> .....	61
3.3.2.3.	<i>Heavy oil</i> .....	65
3.3.2.4.	<i>Chlorine content</i> .....	65
3.3.3.	Longer-term properties .....	68
3.3.3.1.	<i>Corrosion test</i> .....	68
3.3.3.2.	<i>Accelerated aging test</i> .....	70
3.3.4.	Main conclusions of chlorinated plastic pyrolysis .....	74
3.4.	Pyrolysis of newspaper, cardboard and plastic .....	75
3.4.1.	Product yields .....	76
3.4.2.	Products properties .....	77
3.4.2.1.	<i>Gases</i> .....	77
3.4.2.2.	<i>Light oil</i> .....	79
3.4.2.3.	<i>Heavy oil</i> .....	83
3.4.3.	Longer-term properties of pyrolysis oils .....	84
3.4.3.1.	<i>Corrosion test</i> .....	84
3.4.3.2.	<i>Accelerated aging test</i> .....	86
3.4.4.	Main conclusions of paper and plastic pyrolysis .....	91
3.5.	Pyrolysis of biomass and plastic .....	92
3.5.2.1.	<i>Gases</i> .....	95
3.5.2.2.	<i>Light oil</i> .....	96
3.5.2.3.	<i>Heavy oil</i> .....	99
3.5.4.	Main conclusions of biomass and plastic pyrolysis .....	108
4.	CONCLUSION .....	109
5.	SUMMARY .....	111
	References .....	115

# IMPROVING IN CORROSION, TRANSPORTATION AND STORAGE PROPERTIES OF REAL WASTE DERIVED PYROLYSIS OIL

## ABSTRACT

Globally, the energy demand has been steadily increasing. On the other hand, waste accumulation has been imposed as a social and environmental problem and mitigate its harmful impact had become a necessity. Mixtures of real waste plastic, paper (cardboard, newspaper) and biomass were pyrolyzed under mild conditions in a bench-scale batch and horizontal tubular reactor. In order to improve the product properties red mud, calcium hydroxide, and nickel-loaded zeolite catalysts (Ni/ZSM-5 and Ni/SAPO-11) were used for in-situ upgrading of the pyrolysis products. The composition of gases and pyrolysis oils was followed by GC-TCD, GC-FID, HPLC, EDXRFS and standardized methods. It was found that the gas yields could be increased and the oil properties have been improved (higher energy density, higher concentration of branched compounds, lower C/H ratio and lower contaminants) by using different catalyst mixtures. Contaminants from raw materials mainly moved to the gaseous fractions.

Chemical and physical properties involving density, viscosity, solid deposition and the total acid number have been followed as evaluation parameters for assessing the stability and long-term applicability of the waste-derived pyrolysis oils. During the accelerated aging test, the samples were stored in sealed containers for 7 days at 80°C and their properties were measured daily. The corrosion properties of the pyrolysis oil were followed via copper plate storage at room temperature until 60 days. It was established that the waste plastic sourced pyrolysis oils showed considerable higher stability. Contemporaneously, the biomass-derived oil density, viscosity and total acid number have increased significantly due to the presence of oxygenated and unsaturated compounds. Considerably, the aging properties were more advantageous for pyrolysis oils that accomplished by the use of a tubular reactor than that of from batch reactor.

**Keywords:** wastes, pyrolysis, catalysts, stability, improving, aging test

# AMÉLIORATION DES PROPRIÉTÉS DE CORROSION, DE TRANSPORT ET DE STOCKAGE DE L'HUILE DE PYROLYSE DÉRIVÉE DE DÉCHETS RÉELS

## ABSTRAIT

À l'échelle mondiale, la demande d'énergie n'a cessé d'augmenter. D'autre part, l'accumulation de déchets a été imposée comme un problème social et environnemental et l'atténuation de ses effets néfastes était devenue une nécessité. Dans cette étude, un mélange de déchets plastiques réels, déchets papiers (carton, papier journal) et la biomasse ont été pyrolysés dans des conditions douces dans un réacteur tubulaire discontinu et horizontal continu à l'échelle du banc via un processus thermique et catalytique. Afin d'améliorer les propriétés du produit, des boues rouges, de l'hydroxyde de calcium et des catalyseurs zéolithiques chargés de nickel (Ni/ZSM-5 et Ni/SAPO-11) ont été utilisés dans la valorisation in-situ des produits de pyrolyse. La composition des gaz et des huiles de pyrolyse a été suivie par GC-TCD, GC-FID, HPLC, EDXRFs et des méthodes standardisées. Il a été constaté que les rendements en gaz pouvaient être augmentés et les propriétés de l'huile améliorées (rapport mono-aromatique plus élevé, densité d'énergie plus élevée et concentration plus élevée de composés ramifiés, rapport C/H inférieur et contaminants plus faibles tels que les composés chlorés et oxygénés par utilisation de différents mélanges de catalyseurs. Les contaminants provenant des matières premières se sont principalement déplacés vers les fractions gazeuses.

Les propriétés chimiques et physiques impliquant la densité, la viscosité, les dépôts solides et l'indice d'acide total ont été suivies comme paramètres d'évaluation pour évaluer la stabilité et l'applicabilité à long terme des huiles de pyrolyse dérivées des déchets. Pendant l'essai de vieillissement accéléré, les échantillons ont été stockés dans des contenants scellés pendant une semaine (7 jours) à 80°C et leurs propriétés ont été mesurées quotidiennement. En revanche, dans le cas du test de vieillissement non accéléré, les échantillons d'huile ont été conservés dans les mêmes contenants pendant 60 jours à température ambiante et les mêmes paramètres ont été mesurés. Il a été établi que les huiles de pyrolyse d'origine plastique usagées présentaient une stabilité considérablement plus élevée. En même temps, la densité, la viscosité et l'indice d'acide total issus de la biomasse ont augmenté de manière significative en raison de la présence de composés oxygénés et de composés insaturés. De façon considérable, les propriétés de vieillissement étaient plus avantageuses pour les huiles de pyrolyse que celles obtenues par l'utilisation d'un réacteur tubulaire que celles d'un réacteur discontinu.

**Mots-clés:** déchet, pyrolyse, catalyseurs, stabilité, amélioration, test de vieillissement

## ABBREVIATION

ABS	Acrylonitrile Butadiene Styrene
BET	Brunauer-Emmett-Teller
BTU	British Thermal Unit
ELV	End of life vehicles
FCC	Fluid catalytic cracking
FTIR	Fourier Transform Infrared spectroscopy
GC	Gas Chromatography
GDP	Gross domestic product
GPC	Gel permeation chromatography
HDPE	High-density polyethylene
HHV	Higher heating value
HPLC	High-performance liquid chromatography
IEA	International Energy Agency
LDPE	Low-density polyethylene
LHV	Lower heating value
MPY	Mils per year
MS	Mass Spectrometry
MSW	Municipal Solid Waste
Mtoe	Tone of oil equivalent
PA	Polyamide
PC	Polycarbonate
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinyl chloride
SAN	Styrene-acrylonitrile
SEC	Size-exclusion chromatography
TAN	Total Acid Number
WCED	World Commission on Environment and Development
WEEE	Waste Electrical and Electronic Equipment

Veszprém, Hungary, 05.11.2020.

## STATEMENT

Undersigned Fekhar Bahmed hereby declare that the “*Improving in corrosion, transportation and storage properties of real waste derived pyrolysis oil*” titled work has been written within the doctoral program at the University of Pannonia, Doctoral School of Chemical Engineering and Materials Science (at the MOL Department of Hydrocarbon and Coal Processing).

I also declare that the results in the dissertation were the result of my own work, and only the given references in all of the dissertation have to be used. I also followed the rules for reference during the preparation of the dissertation and I have avoided any form of plagiarism.

Fekhar Bahmed



## ACKNOWLEDGEMENT

This work was carried out as part of the research activities at the University of Pannonia, MOL Department of Hydrocarbon and Coal Processing. Begin with, I would like to express my deep gratitude to my supervisor, Dr. Norbert Miskolczi, the Head of MOL Department of Hydrocarbon and Coal Processing, for entrusting me with this subject, as well as for his encouragement, invaluable advice, motivation and regular monitoring without which this work could not have been completed. Thank you for the time you have given me, your guidance and your encouragement during these three years.

Dear Viktória Zsinka, I thank you especially, for your kindness, your availability, and your support. I am delighted to have worked with you.

I would also like to thank all the people (Abdulraheem M., Tomasek Sz., Jónás J., Holló A., Sója J., Visnyei O., Toth O., Eller Z., and those whom I forgot) with whom I had the opportunity to exchange. Thank you for the patience, pedagogy and help.

In addition, I want to express my appreciation to Dr. Aneta Magdziarz and Dr. Gyorgy Polczmann as reviewers for their valuable suggestions to increase the scientific level of the thesis.

I dedicate this work to my dear parents who spared no effort to support me throughout my studies. Moreover, all my friends who have supported me during these three years.

Fekhar Bahmed

## **Introduction**

The utilization of waste polymer is important both from environmental and energetic aspects. Chemical recycling looks a prospective way for long term utilization of waste polymers. Products could be used as feedstocks for refinery, petrochemical processes or chemical synthesis. However, the undesired components in raw materials can deteriorate the product properties, e.g. corrosion, transportation and storage properties of the pyrolysis products. One of the main concerns encountered when using pyrolysis oils is their poor physical and chemical stability [1,2]. The long term properties of the pyrolysis oils can be improved in different ways: pre-situ, in-situ and post-situ. Due to economical and technical reasons, there is a great effort to combine the pyrolysis and product quality improvement steps in the same operation unit and at the same time. However, the selection of catalysts, reaction parameters, or operation units is an important aspect of both the process and product development.

The long term properties of the waste-derived pyrolysis (bio) oils are investigated by accelerated aging tests. Especially the change in the flow properties of the products are followed by their comparison before and after the aging. The physicochemical characteristics of oil change over time and can cause an increase in viscosity and a phase separation [3]. Regarding the corrosion properties, the TAN and metal plate tests have great importance.

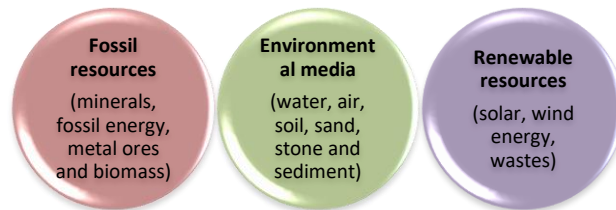
The main aim of this study is to investigate the effect of different raw materials, reactor configurations and catalysts for the in-situ upgrading of pyrolysis oil. Furthermore, the possibility for improvement in corrosion, transportation and storage properties of real waste-derived pyrolysis oil is investigated to obtain valuable hydrocarbons for an energetic, refinery or even petrochemical application. The corrosion, transportation and storage properties of pyrolysis oils were investigated through an accelerated aging test.

# 1. LITERATURE SUMMARY

## 1.1. Resources, wastes, energy consumption and sustainability

### 1.1.1. Resources

Human life has been dramatically depending on the natural resources for 200,000 years when life had been beginning on Earth. However, well shown a massive increase in energy and resource dependence has been demonstrating especially since the industrial revolution in the XVIII century. On the other hand, civilization and modern societies cause numerous problems; e.g. exhausting the natural resources (especially fossils), destroying nature, polluting the air which is considered as irreversible changes in the climate [4–7]. The natural resources are physical assets, which can not be obtained by artificially and are useful to humans. The natural resources could be classified according to *Figure 1.1*.



*Figure 1.1*  
The natural resources

Regarding the fossil resources, they include minerals, fossil energy, metal ores and biomass, which are required for most human activities. Fossil energy, metal ores and minerals are non-renewable. On the other hand, biomass including agricultural crops (fast-renewing resources) and wood (slow-renewing), which are renewable within the human time scale. The environmental media (e.g. water, soil, air, sand, rock, stone, sediment, etc.) has a considerable impact on sustainability on the Earth, and the loss of quality remains the main source of concern. Renewable resources can not be exhausted but other inputs or resources are needed to exploit them [8].

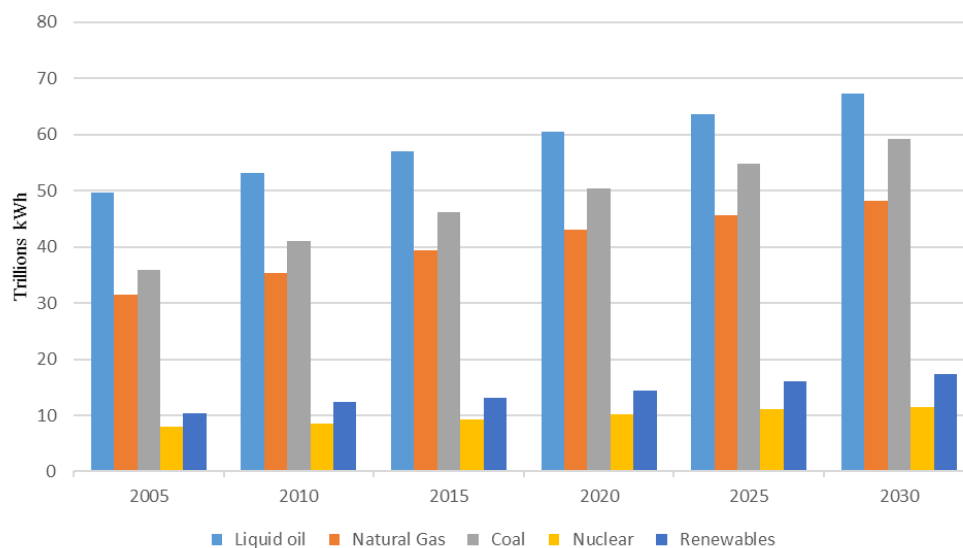
### 1.1.2. Energy consumption and sustainability

Energy has crucial importance for the economy, industry, and most aspects of human life. The energy consumption of the World increased in the past and according to the forecasts, it has an increasing tendency in the future. However, the energy consumption

is fundamentally affected by the population, GDP increasing, society, industrial development, etc. Nowadays the main energy sources are still fossil-based, however great difference could be observed regarding the different regions [9–11].

The World's primary energy consumption was around 13,9 Mtoe in 2017 according to the IEA. This consumption was 81% based on fossil sourced (32% for oil only). On the other hand, the importance of fossil energy sources is declining very slowly (e.g. it was 87% in 1973 and 84% in 2018) [12–14].

The global CO<sub>2</sub> emissions from energy combustion reached 32.8 Gt in 2017, which was more than double that of the 1973 level (15.5 Gt CO<sub>2</sub>). The EIA estimates that the increase in global energy consumption will be the consequence of the strong economic and demographic growth in developing countries, therefore 46.9% increasing in energy consumption is predicted between 2018 and 2050 [15,16] (*Figure 1.2*).



**Figure 1.2**  
The global energy consumption [16]

The sustainable development or sustainability is defined as follows: *"Sustainable development is the development that meets the needs of the present without compromising possibility for future generations to be able to respond to their own needs"* [17]. In 1989, the Report was the subject of a debate at the United Nations General Assembly, which consequently decided to organize a United Nations Conference on Environment and Development [18].

From the energy and waste aspect, sustainability has a close connection with the waste hierarchy: preventing, reuse, recycling and recovery [19]. However, the reduction,

storage and utilization of harmful components is covered by the area of sustainability; improving in energy and material efficiency and process design; material/energy substitution or materials from renewable sources; sustainable energy holders, or even sustainable waste management (*Figure 1.3*).



**Figure 1.3**  
Environmental sustainable development [16]

The long-term recycling of waste is not only an aspect of sustainability but also of energy security or environmental protection. In addition to reducing waste, optimized waste management and advanced technologies are also key factors [20,21]. One of the key issues for sustainability is how we can provide the energy needed for the population. Due to the limited availability of fossil energy sources and the environmental problems caused by their usage, the research and application of alternative, cleaner and sustainable energy sources have an important role [22,23].

### 1.1.3. Wastes

The term "wastes" is described by many definitions. When something loses its primary function for a user, it will become waste; however, the waste of one can serve as secondary raw materials for the manufacture of other products and even goods for other people or communities. From the economic point of view, waste is defined as an object or a material with an economic value of null or negative [22]. This is relative to the state of the technological art and the location of its generation. In recent years, waste tends to become a valuable product, e.g. they can be used as raw materials or energy sources for further up to date processes. Furthermore, waste reusing and recycling is one of the key elements of the circular economy.

There are many classifications for wastes, but they are not universal. They can be classified in different ways according to the objectives and interests (**Figure 1.4**). A very detailed classification of the waste according to their origins is made by The *Encyclopedia “les Techniques de l’ingénieur”* [23].



**Figure 1.4**  
Classification of wastes [23]

Wastes should be accidental (inevitable dysfunctions of production and consumption systems), biological, chemical (by-products or unusable products of chemical reactions), ecological (very close to the pollution and environmental aspects), economical (close connection with the durability of products, objects and machines generate a loss in the market and economy) or technological (rejected items, mass flows from different processes).

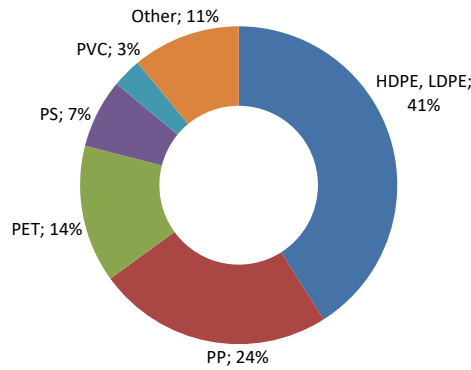
## **1.2. The problems of waste polymers**

Polymers should be natural or artificial origin: plastics, biomass, paper, rubber, bone, etc. The environmental issues of the polymers are in the focus of waste management, because of their unfavoured decomposition properties.

### **1.2.1. Plastic**

Nowadays plastics are important materials in many sectors; e.g. packaging, textiles, toys, sports goods, electrical and electronic appliances, etc. The global plastic production is 350 million metrics tons, with an annual growth rate of around 5% [24]. Most of the plastics are obtained from non-renewable fossil sources [25]. Based on statistical data, the average composition of waste plastics are 41% LDPE and HDPE, 24% PP, 14% PET,

7% PS, 3% PVC and 11% others (**Figure 1.5**) [26,27]. However, the composition of waste plastics is considerably affected by the application area. Waste plastic from the packaging sector consists of dominant polyolefins (HDPE, LDPE, PP), WEEE has mainly ABS, PS, PC, SAN, ELV plastic waste contain PP, PA, ABS, PS, PUR, while plastic waste from civil engineering and construction has a vast amount of PVC, PS and PUR [27,28].



**Figure 1.5**  
The composition of plastic wastes [26,27]

The major problem with waste plastics is that they can not be degrading due to their unique structure. As a result, plastics reaching the end of their life cycle and released into the environment are accumulated everywhere. However, waste plastics are valuable secondary raw materials because of their high-energy content. This means that significant energy and release pollutants into the environment can be saved by their proper recycling. In addition to degradation problems, the heterogeneous composition of waste plastics and the problem of selective sorting are considered as the main difficulties [29].

### 1.2.2. Biomass

Biomass is a generic term for organic matter; biological, living or dead plants that are partially integrated into the ecosystem can be used for energy purposes [30]. Due to the negative CO<sub>2</sub> emission, biomass not participates in global warming [31]. It is well known, that the energy of the sun is used to convert carbon dioxide and water into biomass in a process known by photosynthesis. The yearly amount of the generated waste biomass is around 170 billion tons and the largest proportion of biomass is lignocellulose [32]. The biomass structure contains cellulose (about 50%), hemicelluloses (about 25%) and lignin (about 25%), while it has small amounts of mineral matter. Their proportions can be extremely depending on the plant, age and growing conditions, soil, climate, fertilizers, etc. [33]. The main compositions of the different biomasses are summarized in **Table 1.1**.

**Table 1.1**  
The main properties of biomass [34]

	Cellulose, %	Hemicellulose, %	Lignin, %	Extractive substances, %	Ash, %
<b>Hardwood</b>	39	35	20	3	0.3
<b>Peat</b>	10	32	44	11	6.1
<b>Pine bark</b>	34	16	34	14	2.0
<b>Rice husk</b>	30	25	12	18	16.1
<b>Softwood</b>	41	24	28	2	0.4
<b>Wheat straw</b>	40	28	17	11	7.2

The different proportions of the constitutions in biomass led to differences in moisture content, calorific value, fixed carbon and volatile matter, mineral content, etc. These differences are fundamentally affecting the further utilization of biomass, especially for energy purposes [35–37].

One of the biggest problems with biomass is that every year a significant amount of biomass is generated, especially in agriculture, which reusing is not solved. *Table 1.2* summarizes the biomasses with the highest amount from different sources.

**Table 1.2**  
The main sources of biomass and their properties

Biomass	C, %	H, %	O, %	N, %	LHV (MJ/kg)	Ref
<b>Peanut shell</b>	56.5	6.6	35.3	1.5	18.5	[40]
<b>Palm shell</b>	54.4	7.5	35.6	2.0	21.5	[41]
<b>Cashew shell</b>	56.4	7.1	33.5	0.6	21.9	[42]
<b>Millet stalks</b>	51.6	6.4	40.6	1.3	18.1	[43]
<b>Sorghum stalks</b>	46.1	5.8	40.3	0.4	16.6	[43]
<b>Corn stalks</b>	44.0	6.3	41.8	0.8	14.9	[44]
<b>Rice husk</b>	42.8	4.5	29.3	0.4	14.9	[45]
<b>Cotton stalks</b>	49.4	6.3	43.5	0.8	16.7	[46]
<b>Bituminous coals</b>	85.0	5.0	7.0	1.8	34.1	[47]

In many places, this type of waste biomass is simply incinerated, causing significant air pollution problems. The other significant waste biomass source is the biomass part of the municipal solid waste, which further value-added utilization is not currently solved [38,39].



### 1.2.3. Paper

Chemically, paper and cardboard are kinds of biomass, because of their cellulose content. Recently at least three main types of paper are used worldwide: paper for newspaper, books, copy machine or printers, the cardboard and paper for other purposes (e.g. sanitary paper, napkin, packaging paper, etc.). The annual production of paper is around 400 million tonnes [48]. The main properties of the most used papers are summarized in *Table 1.3* [49].

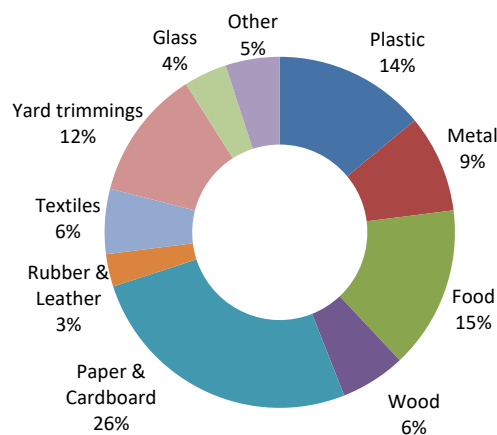
**Table 1.3**  
The main properties of the paper and cardboard [49]

	C, %	H, %	O, %	N, %	Ash, %	Fixed carbon	Volatiles, %
<b>Paper</b>	39.4	5.4	44.6	0.6	10.0	17.0	68.0
<b>Cardboard</b>	40.6	5.7	47.2	0.5	6.0	18.0	71.0

There are several methods of recycling or reusing paper waste. On the other hand, paper waste that is not selectively collected and found mixed with other wastes can cause significant problems. Due to the high efficiency of the paper sorting, a vast amount of papers are recycled [50]

### 1.2.4. Municipal Solid Waste

The municipal solid waste is a mixture of different materials containing mainly cellulose. The composition of MSW is shown in *Figure 1.6* [50].



**Figure 1.6**  
The composition of MSW [50]

As the figure shows, MSW consists of mainly biomass wastes (~1/3 part of the MSW) and paper which are made of cellulose. According to statistics, approximately 3.5

billion tonnes of MSW are generated worldwide each year [51]. The main properties of MSW are summarized in **Table 1.4** [52]. The composition of MSW varies greatly depending on countries, regions, living standards, economic conditions, environmental development, etc. One of the biggest problems with MSW is the heterogeneity and variable composition, which significantly limits the deployment and technical-economic characteristics of a given technology. The elementary composition of raw materials is useful because it helps to anticipate the chemical and physical properties of the pyrolysis products.

**Table 1.4**  
The main properties of MSW [52]

	C, %	H, %	O, %	N, %	S, %	Ash, %
<b>Paper</b>	43.5	6	44	0.3	0.2	6
<b>Plastics</b>	60	7.2	22.8	-	-	10
<b>Food waste</b>	48	6.4	37.6	2.6	0.4	5
<b>Ward waste</b>	47.8	6	38	3.4	0.3	4.5
<b>Textiles</b>	55	6.6	31.2	4.6	0.2	2.5
<b>Rubber</b>	78	10	-	2	-	10
<b>Wood</b>	49.5	6	42.7	0.2	0.1	1.5
<b>Glass</b>	0.5	0.1	0.4	≤0.1	-	98.9
<b>Metal</b>	4.5	0.6	4.3	≤0.1	-	90.5
<b>Dust, ash</b>	26.3	3	2	0.5	0.2	68

### 1.3. Processes for waste polymer utilization

#### 1.3.1. Landfilling

Landfilling consists of monitoring, depositing and compacting the waste [53]. However, this option of management by ultimate storage is also associated with negative impacts on the environment and risks to public health, due to the multiple activities that take place at the landfill site and the products that are released to the environment.

The main products of the landfill process are landfill gas and leachate. Landfill gases are mainly the consequence of microbial degradation of waste or the chemical reactions within the different waste components. Because of the landfill gas including methane and carbon dioxide, it is responsible for more than 18% of global warming [54,55]. Moreover, landfill gas also contains other trace gaseous elements that can be toxic, even at low concentrations. The combustible gas can be recovered as an energy source.

The leachate produced by the landfill process contains a significant amount of organic matter in solution and suspension; ammonium ions and inorganic ions, which can cause environmental risks [56]. Depending on the operation conditions, numerous ways of waste treatment are implemented, thus contributing to the environmental and health harmfulness linked to storage. The uncontrolled release of leachate can percolate to groundwater or migrate to surface water [57].

### **1.3.2. Mechanical recycling**

The mechanical recycling of plastic wastes consists of many steps from sorting to shaping. This type of waste utilization is advantageous for non-contaminated, highly selectively collected waste plastics [51]. One of the most disadvantageous of mechanical recycling, that mixture of plastic wastes is not recycled or even the interfacial forces must be improved by surface modifying additives e.g. by compatibilizers. The compatibilizers can efficiently create a physical or chemical linkage between the different plastic constituents of the polymer blends [52,58]. The recycled materials often have lower value and worst properties than the original (downcycling). On one hand, most of the selectively collected plastic from packaging is mechanically recyclable, however, they have some limitations [59]. One of the most limitation for mechanical recycling is the low efficiency in selective waste collection and separation, the high raw material price, the non-compatible constituents or even the customer acceptance of the recycled products.

### **1.3.3. Chemical recycling by solvents**

The chemical recycling is a depolymerization process when the long chains of the polymers (e.g. plastic, biomass, etc.) are decomposed under certain conditions. In the case of the chemical initiated decompositions, the elementary part of the polymers (e.g. plastics) can be recovered. Depending on the nature of these plastics, chemical recycling can take different forms. In the case of dissolution, the polymer chains can be recovered by solvent [60].

### **1.3.4. Thermal processes**

Polymer wastes can be utilized by thermal processes; incineration, gasification or pyrolysis depending on the parameters. The oxidizing of solid waste by combustion is called as incineration. Gasification is also an oxidizing process, but the temperature is

higher than in the case of incineration and the main product is the gaseous fraction. The pyrolysis of wastes is a process exclusion of oxygen or air.

#### **1.3.4.1. Incineration**

The incineration of MSW can reduce the volume of waste by approximately 90%, and recover most of the energy contained in it (about 2,300 kWh/t) [60]. The non-combustible substances (metals, glass, ceramics, minerals and inorganic matter, etc.) are found in slag and incineration residues, which are potentially hazardous residuals [62]. According to Kim et al., fly ash contains a large proportion of particles between 1 and 100  $\mu\text{m}$  [63]. The main inorganic contaminants are As, Cd, Hg, Mo, Pb and Zn [64,65]. The presence and concentration of these contaminants depend on the type of residue [66], the composition of incinerated waste and technology [67].

#### **1.3.4.2. Gasification**

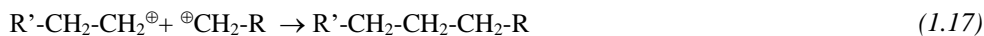
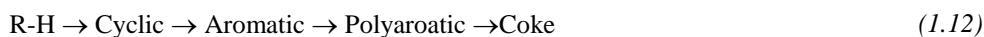
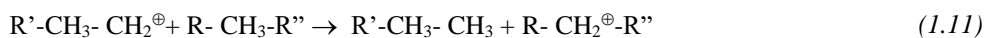
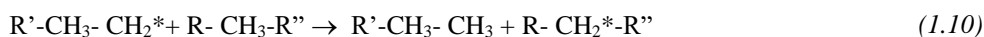
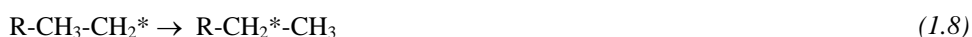
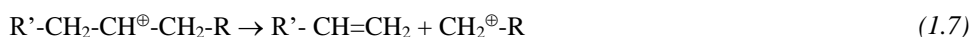
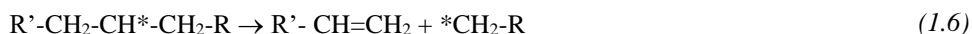
Gasification is partial oxidation of wastes at a temperature between 800-1300°C. Gasification generates mainly  $\text{H}_2$ , CO and  $\text{CO}_2$  [68]. Due to the presence of water (mainly from biomass and paper raw material) and the in-situ generated  $\text{CO}_2$ , the oxidation reactions in the presence of water vapor or  $\text{CO}_2$  are endothermic, whereas that of with oxygen is exothermic (1.1-1.3) [68-70].



The main purpose of the gasification of solid biomass, paper or plastic is the synthesis gas production, mainly composed of  $\text{H}_2$ , CO,  $\text{CO}_2$ ,  $\text{CH}_4$  and other light hydrocarbons [71]. The synthesis gas must be cleaned to remove small particles, alkali metals, tars, condensable hydrocarbons and other contaminants, then it can be used e.g. for energy generation, fuel and base oil production (Fischer-Tropsch synthesis), chemical synthesis, hydrogen production, ammonia production, methanol production, etc. [72]. The calorific value of the synthesis gas is in the range of 4-6  $\text{MJ}/\text{Nm}^3$  depending on the gas composition [70,73].

### 1.3.4.3. Pyrolysis

Pyrolysis is a thermal conversion that takes place in the absence of oxygen led especially to the cracking of C-C bonds and rearranging the bonds of the products [74]. Depending on the reaction conditions and raw materials the main products of the pyrolysis are gases (mainly CO, CO<sub>2</sub>, H<sub>2</sub> and C<sub>1</sub>-C<sub>3</sub> hydrocarbons), condensables (bio-oil, tars, etc.) or solid char [75–77]. The degradation of molecules is caused by the dissociation of chemical bonds and the production of free radicals [78]. The simplified reactions are summarized in (1.4-1.18).



The way a molecule fragments during pyrolysis and the identity of the fragments produced depends on the type of chemical bonds involved and the stability of these fragments. The chain of most synthetic polymers will break more or less randomly to produce smaller molecules [79,80]. The primary reactions consist of char formation, depolymerization and fragmentation [81]. During the primary depolymerization reactions, the raw material cracks into smaller fragments, which give volatiles and gases [82,83]. In the secondary reactions, the primarily formed compounds might not be stable can still go

through cracking and/or recombination reactions [84]. From cracking of the primary molecules, lighter combinations will be produced while the recombination will give rise to the creation of heavier compounds or deposit on external char [85,86].

Depending on the operation conditions, the pyrolysis process can be classified into conventional (slow) pyrolysis and rapid pyrolysis [87]. Pyrolysis vapors do not escape as quickly as in rapid pyrolysis. Thus, the components in the vapor phase continue to react with each other. Therefore the main product is the pyrolysis oil in case of fast pyrolysis, while typically more amount of gases and char could be obtained from slow pyrolysis. The heating rate in conventional pyrolysis is generally less than that of in rapid pyrolysis. The raw material can be kept at a constant temperature or heated slowly and the vapors can be removed continuously as they are formed. Rapid pyrolysis is a high-temperature process in which polymer is rapidly heated in the absence of oxygen [88,89].

Catalysts have a key role in the pyrolysis. The catalyst-free thermal pyrolysis requires relatively high temperatures; the products are characterized by high molecular weight and very wide distribution of the carbon chain with high acidity and viscosity [90–92]. Depending on the raw materials, pyrolysis oils contain acids, aldehydes, ketones, aromatics and alcohols that can limit its use. Catalysts can improve product quality. The most commonly used catalysts are HZSM-5, HUSY and H $\beta$  [93,94], silica-alumina, MCM-41 [95], clay [96], metal oxides [97], calcium oxide [98] and calcium hydroxide [99]. The cracking capacity of the catalysts depends both on their physical characteristics (textural properties) and chemical properties (acidic sites). Due to high acidity and shape selectivity zeolites can promote the cracking of C-C bonds and determine the chain length of the products obtained [100]. Zeolites are described as crystalline aluminosilicate natural or synthetic sieves with open pores and ion exchange capacities. Their artificial synthesis has developed for their specific adsorption, catalysis and ion exchange properties [101]. The structure of zeolites is based on a three-dimensional arrangement of TO<sub>4</sub> ([SiO<sub>4</sub>]<sup>4-</sup> and [AlO<sub>4</sub>]<sup>5-</sup>) tetrahedron linked by their oxygen atoms [102].

#### **1.4. Waste polymer pyrolysis for oil production**

The low-temperature pyrolysis and co-pyrolysis using different feedstocks have practical importance for the production of liquid hydrocarbons. Generally 350-400°C is used for low temperature and 400-600°C for mild process depending on the pyrolysis process. The reaction/residence time is varied depending on the type and amount of the

raw material, or even the pyrolysis process. Generally higher operation temperature needs less reaction/residence time.

### 1.4.1. Materials

#### 1.4.1.1. Plastic

Several researchers have shown that plastics have a high perspective to produce an enormous amount of liquid oil via pyrolysis process [103]. **Table 1.5** summarizes the relationship between the pyrolysis oil yield and reaction conditions.

**Table 1.5**  
Pyrolysis oil by waste plastic pyrolysis

Raw material	Pyrolysis oil, %	Gases, %	Char, %	Process	Main parameters	Ref
LDPE/HDPE	84.3/97.7	15.1/0.9	0.0/0.8	Thermal/ Catalytic (5 % mordenite)	700°C/450°C Fixed-bed (batch) reactor	[104,1085]
PP	64.9	24.7	10.4	Catalytic (5% silica-alumina)	380°C Fixed-bed (batch) reactor	[106]
PS	89.5	9.9	0.6	Thermal	580°C Fluidized-bed reactor	[107]
PVC	6.3	84.6	9.1	Catalytic (Activated carbon with different contents of iron)	520°C Fluidized-bed reactor	[108]
PA	56.8	39.2	0.6	Thermal	760°C Fluidized-bed reactor	[107]
PET	41.3	38.7	15.6	Thermal	700°C Fixed-bed (batch) reactor	[109]
PU	50	33	17	Thermal	1000°C fixed-bed reactor	[110]
PC	46.4	26.5	24.6	Thermal	710°C Fluidized-bed reactor	[107]
Polyester	40.0	50.8	7.1	Thermal	768°C Fluidized-bed reactor	[107]
MPW	50	34	16	Catalytic (50% Natural zeolite)	450°C two stage batch reactor	[111]

The pyrolysis oils obtained by plastic waste contains mainly hydrocarbons, which composition is the dependence of raw material and reaction conditions. In the case of non-contaminated plastic waste, the value of pyrolysis oil is significantly high. For energetic purposes especially polyethylene, polypropylene and polystyrene derived pyrolysis oils are favoured because they are free from any form of the elements excluded carbon

and hydrogen. Regarding the hydrocarbons in pyrolysis oils, they contain especially aliphatic saturated and non-saturated hydrocarbons, branched hydrocarbons, cyclic and aromatic compounds.

Ahmad et al. demonstrated that the pyrolysis of HDPE and PP by using a micro steel reactor at 300-400°C resulted in a liquid yield of 81% in the case of HDPE, while 70% using PP at 300°C [112]. Bagri and Williams found high oil yield (95%) with low gas and char yield in case of LDPE pyrolysis in a fixed-bed reactor at 500°C till 20 min [104,105]. High liquid oil yield (93%) has also been attained by Marcilla et al. in a batch reactor at 550°C, with a lower heating rate (5°C/min) [113].

Sakata et al. have reported 80% liquid pyrolysis oil and 6% gas yield in the case of PP pyrolysis at a temperature of 380°C [114]. On the other hand, Fakhrhoseini and Dastanian found a higher liquid yield of oil (82%) when accomplished PP pyrolysis at 500°C [115]. However, a further rise in temperature (over 500°C) can reduce the liquid yield. This was confirmed by Demirbas who conducted the PP pyrolysis at a temperature of 740°C in a batch reactor which leads to 49% liquid yield, 50% gaseous and 1% char [116]. Onwudili et al. have examined the pyrolysis of PS in a batch pressurized autoclave reactor at the range 300 to 500°C for a one-hour period under 0.31 MPa to 1.6 MPa. They found that the pyrolysis resulted in a very high liquid oil yield (97.0%) at an optimum temperature of 425°C [117].

#### **1.4.1.2. Biomass**

Many researchers studied the reaction pathways of biomass into liquid fuel. Three key mechanisms are reviewed for pyrolysis of biomass containing char formation, depolymerization and fragmentation [118]. **Table 1.6** summarizes the relationship between the pyrolysis oil yield and reaction conditions. Besides, to the reaction kinetics and reaction mechanism, understanding the correlation of the product distribution with the process parameters in the case of biomass pyrolysis is also a key area. The pyrolytic gas contains hydrogen, carbon monoxide, carbon dioxide, low carbon number hydrocarbons, SO<sub>x</sub>, NO<sub>x</sub>, etc. Pyrolysis oil as a dark brown liquid is the principal product, which contains hydrocarbons, ketones, aldehydes, phenols, alcohols, esters, furans, alkenes, oxygen or even nitrogen compounds. The oxygenated and unsaturated compounds result in high thermal instability, and low heating value [119,120]. Pyrolysis oil is a multiphase micro-



emulsion contains more or fewer solids (<0.5 wt%) comprising condensed carbon residual material, metals and sand [121,122]. The produced pyrolysis oil yield from biomasses is normally in the range of 50-75%. Generally, higher cellulose content increases the yields of pyrolysis oil [123]. An enormous number of reactions occur during the biomass pyrolysis, including isomerization, depolymerization, dehydration, aromatization, and decarboxylation or even coke formation [124–126].

**Table 1.6**  
Pyrolysis oil obtained from biomass (catalyst-free thermal pyrolysis)

Raw material	Pyrolysis oil, %	Gases, %	Char, %	Main parameters	Ref
Willow	59	23	18	Auger reactor 450°C	[127]
Wood	60	13	27	Centrifugal reactor 575°C	[128]
Straw	43	20	37	Centrifugal reactor 575°C	[128]
Lignin	39	35	26	Centrifugal reactor 575°C	[128]
Algae	57	19	24	Centrifugal reactor 575°C	[128]
Rice straw	44	36	20	Cicrowave reactor (600°C)	[129]
Sugarcane bagasse	43	40	18	Microwave reactor (600°C)	[129]
Coffee grounds	43	35	21	Mcrowave reactor (600°C)	[129]
Bamboo leaves	44	34	22	Microwave reactor (600°C)	[129]
Pennisetum grass	45	33	22	Microwave reactor (600°C)	[129]
Leucaena wood	45	39	16	microwave reactor (600°C)	[129]
Eastern tree species	55	27	18	Vacuum reactor (450°C)	[130]
Hardwood shavings	63	13	24	Fluidized bed reactor (500°C)	[131]
Birch	54	20	26	Vacuum reactor (450°C)	[132]
Lodgepole pine	55	27	18	Two-step vacuum reactor (450°C)	[130]
White spruce+balsam fir	45	27	28	Vacuum reactor (450°C)	[133]
Spruce wood	40	29	32	Horizontal cylindrical reactor (750°C)	[134]
Corn stover	55	16	32	Free-fall fast pyrolysis reactor (500°C)	[135]
Corn stover	31	15	37	Batch pressure reactor (500°C)	[136]
Wheat straw	46	7	47	Circulating fluidized bed (400°C)	[137]
Soybean cake	30	25	25	Fixed-bed reactor (550°C)	[138]
Switchgrass	57	22	21	Pressure reactor (600°C)	[139]
Switchgrass	61	11	28	Fluidized bed reactor (600°C)	[140]
Soybean	26	51	23	Fixed-bed reactor (400°C)	[141]
Soybean cake	59	18	23	Fixed-bed reactor (550°C)	[142]
Corn stover	62	22	17	Fluidized bed reactor (550°C)	[143]

### 1.4.1.3. Paper

The waste paper contains typically hemicellulose and cellulose [144,145]. The attention in pyrolysis of wastes papers has augmented in latest years as it offers an option for thermal upgrading of waste to higher calorific value hydrocarbon. **Table 1.7** summarizes the relationship between the pyrolysis oil yield and reaction conditions.

**Table 1.7**  
Pyrolysis oil obtained from paper (catalyst-free thermal process)

Raw material	Pyrolysis oil, %	Gases, %	Char, %	Main parameters	Ref
Paper sludge	40	19	41	Horizontal tubular reactor (400°C)	[149]
Paper sludge	37	31	32	Horizontal tubular reactor (700°C)	[149]
Waste paper	46	39	15	Horizontal tubular reactor (390°C/10°C min <sup>-1</sup> )	[146]
Waste paper	47	37	16	Horizontal tubular reactor (420°C/10°C min <sup>-1</sup> )	[146]
Waste paper	47	35	18	Horizontal tubular reactor (450°C/10°C min <sup>-1</sup> )	[146]
Waste paper	49	34	17	Horizontal tubular reactor (420°C/30°C min <sup>-1</sup> )	[146]
Waste paper	48	33	19	Horizontal tubular reactor (450°C / 30°C min <sup>-1</sup> )	[146]
Waste paper	56	20	24	Fixed bed reactor (550°C /1.0°C/s)	[150]
Waste paper	47	26	27	Fixed bed reactor (550°C /0.1°C/s)	[150]
Paper cup waste	42	27	31	Semibatch reactor (425°C/30°C min <sup>-1</sup> )	[151]
Paper cup waste	30	27	43	Semibatch reactor (325°C/30°C min <sup>-1</sup> )	[151]
Paper mill sludge	36	24	40	Batch reactor (500°C/10°C min <sup>-1</sup> )	[152]
Waste office paper	42	15	43	Rotative microwave reactor (<200°C)	[153]
Pulp and papermaking sludge	24	30	46	Tubular furnace reactor (800°C/20°C min <sup>-1</sup> )	[154]
Paper sludge	40	24	36	Tubular furnace reactor (500°C/10°C min <sup>-1</sup> )	[149]
Paper sludge	37	31	32	Tubular furnace reactor (700°C/10°C min <sup>-1</sup> )	[149]

Pyrolysis oils from paper wastes have been before seen as fuel for direct combustion [146]. The biogas produce from paper waste pyrolysis has practical calorific energy, which can be combusted to deliver the necessary internal heat of pyrolysis reactor. At 500°C approximately 40% of the dry paper sludge weights can transform into liquid oil. On the other hand, the waste papers (e.g. paper and cardboard) is typically do not pyrolyzed alone, because in the case of selectively collected paper wastes they are recycled by mechanically. Regarding pyrolysis, the mixtures of different wastes containing paper have an important aspect [147,148].

### 1.4.2. Co-pyrolysis

The co-pyrolysis is widely used for improving the oil yield. Especially the co-pyrolysis of plastics and other wastes (e.g. coal, biomass, paper, etc.) are investigated [155]. Biomass can enhance the liquid yield in the case of the pyrolysis of plastic and biomass, however, especially the water content and the yield of unflavoured acidic components can increase significantly [156–158]. The energy content of the liquid oil significantly decreases, and the energy produced from the co-pyrolysis of biopolymers is lower comparing that of to the fossil sourced plastics [159,160].

Regarding the pyrolysis oil, an increasing yield was found (46.13 → 61.63 wt %) by the adding of PS to palm shell using a temperature of 500°C [157]. Furthermore, the quality of oil can be upgraded when PS was used during the pyrolysis. E.g., the HHV can be also increased from 11.94 MJ/kg to 38.01 MJ/kg as a function of PS concentration. A similar result was concluded by Brebu et al, who investigated the co-pyrolysis of synthetic polymers (PP, LDPE and PS) with pinecone at 500°C. Furthermore, the energy contents of oils in the case of the co-pyrolysis were higher than those of the pyrolysis of pinecone [156].

The application of biopolymers in co-pyrolysis has also high importance. PLA, PHB, etc was pyrolyzed using semi-continuous pyrolysis reactor, under nitrogen, and the temperature of 450°C [127,161,162]. They found that due to the synergetic effect, the water content can be reduced in pyrolysis oil, while the pyrolysis oil yield and the heating value were also higher. PHB has the most benefits for the pyrolysis, because of the highest oil yield and heating value [163].

Both synergistic and antagonistic effects can be found through radical interactions during the co-pyrolysis process. Negative or positive effects depending on the type and contact of components were demonstrated during the pyrolysis. The heating rate, final temperature, catalysts and type of hydrogen-donors are the main factors that can considerably affect the synergistic effects [164–168]. Others found, that due to the more hydrogen in biomass it could play as a hydrogen donor to WEEE decomposition during the co-pyrolysis [185]. Water is one of the main constituents in biomass and can act as a reactive compound to stimulate further cracking of plastic waste to increase the pyrolysis oil yields [169,170]. On the other hand, the mechanism of the synergistic effect between plastic and biomass during their co-pyrolysis is unclear.

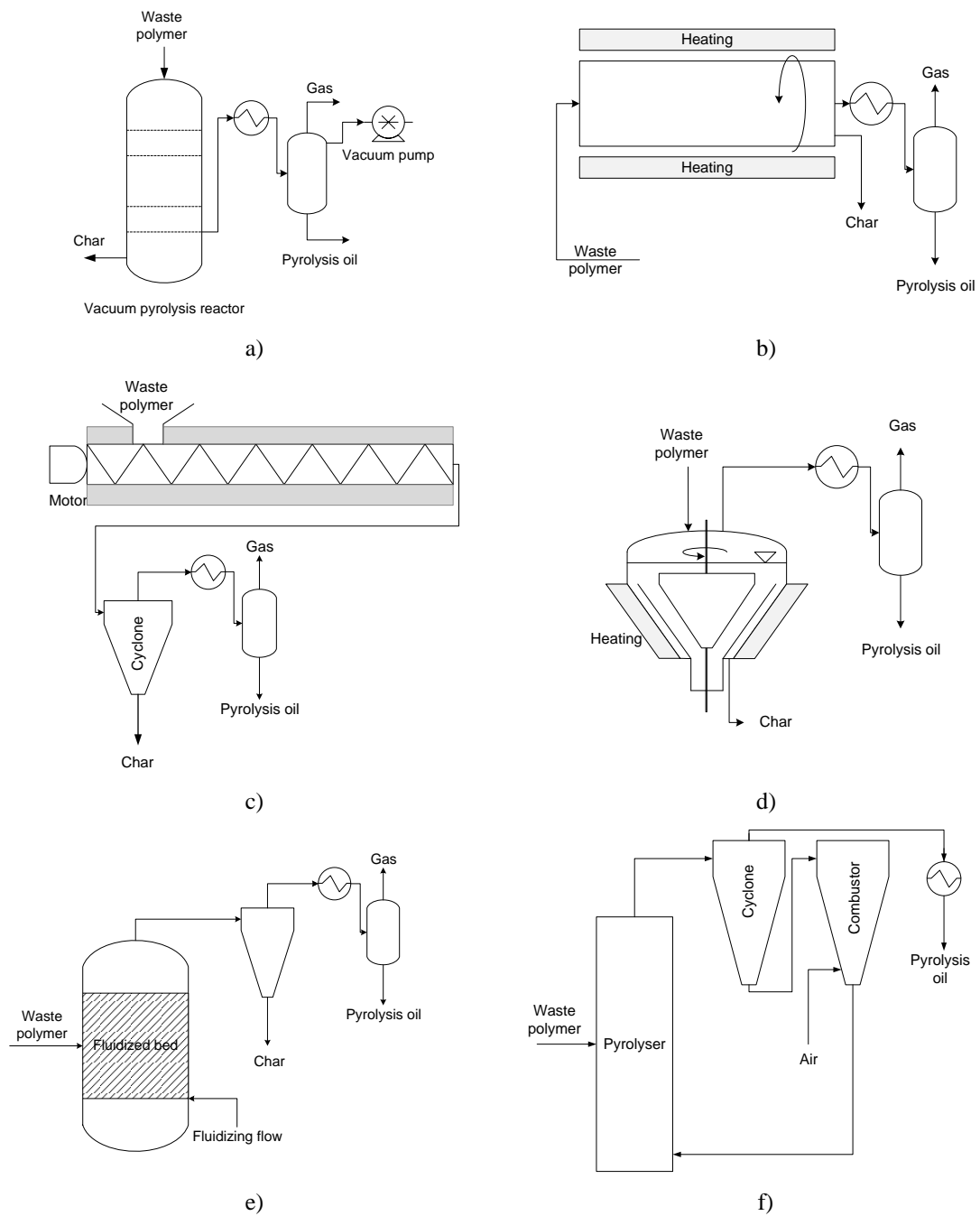
Plastic and biomass have dissimilar decomposition mechanisms during the thermal pyrolysis procedure through a series of endothermic and exothermic reactions (initiation, propagation, and termination) [177,172]. Biomass has less thermal stability than plastics, which can affect their radical degradation mechanism by supporting the degradation of synthetic macromolecules [173,174]. This observation was supported by Sun et al during the co-pyrolysis of wood, poplar, and HDPE in a micro-scale reactor [175,176]. Free radicals from biomass obtained at lower temperatures can contribute to reactions of plastic decomposition, increasing the yield of volatiles. The synergistic or antagonistic effects in co-pyrolysis are multifaceted because of numerous chemical species [177].

Pyrolysis of paper results significant amount of oxygen-containing compounds, which can be the source of many problems during the further application of products. In some cases, it is difficult to separate the paper from the plastic waste. Therefore, the co-pyrolysis of paper and plastic is also investigated segment [178-183]. However, the presence paper in raw materials, had a considerable effect to the product yield and quality. For example in case of the co-pyrolysis of paper and polystyrene, the presence of excess hydrogen from cellulose decomposition can enhance the hydrogenation of styrene monomers [178]. In case of the stepwise pyrolysis of mixed paper and plastics waste in a batch fixed bed reactor at 350 and 500 °C resulted acidic products and oxygenated compounds, but they were concentrated in the liquid products obtained from the first step [179]. Lopez et al. reported significant dechlorination of the products, in case of the pyrolysis of municipal solid waste rich in paper [180]. Brown et al investigated the slow pyrolysis of paper and different plastic mixtures. They found, that deoxygenation of paper constituent can resulted higher caloric value in char and rather tar product was obtained at lower temperature [182]. It was also demonstrated, that less greenhouse gas emissions was found in case of pyrolysis of paper and plastic mixtures than in their landfill [183].

### **1.5. Pyrolysis reactor configurations**

There are many types of the reactors for waste pyrolysis. General characteristic of the reactors, that they requires rapid transfer of heat from the environment into the degraded waste polymers. Therefore the main developments are focus to the heat transfer optimization. It should be realized by gas or heat transfer material; e.g. inert gas or water vapor, metal balls, sand, molten metals, molten salts. Furthermore advanced heat transfer can be reach by direct heating using contact with the inner reactor walls. *Figure 1.7* summarizes

the main recently development in reactor configurations [40,74,76,104,117,136,137,140, 209,225,248,289].



**Figure 1.7**

Different pyrolysis reactor configurations

(a) batch reactor (with or without vacuum), b) rotary kiln reactor, c) screw/auger reactor, d) rotating conical reactor e) fluidized bed reactor, f) circulating fluidized bed reactor)

## 1.6. Product properties of the waste polymer pyrolysis

The decomposed products of the waste polymer pyrolysis are separated into different fractions (gases, pyrolysis oil) mainly by condensation and phase separation. The solid char is accumulated in the bottom fraction or it should be separated by filtration. The pyrolysis oil can be further separated by atmospheric distillation into hydrocarbons with different boiling ranges; e.g. light oil, middle distillate, heavy oil.

### 1.6.1. Gases

Non-condensable gases produced by the pyrolysis of polymers consist of hydrocarbons, carbon monoxide, carbon dioxide and hydrogen and others. Pyrolysis of polyethylenes, PP, PS and other plastics containing only carbon and hydrogen in the macromolecule results in hydrogen and hydrocarbons. On the other hand, chlorinated compounds, CO, CO<sub>2</sub> and compounds containing nitrogen can be also detected in the gaseous fractions in case of the thermal decomposition of plastic containing chlorine (e.g. PVC), oxygen (e.g. PET), nitrogen (e.g. polyamides). Gases can be used as fuel for combustion purposes or as a fluidizing medium or/and carrier gas for a fluidized bed reactor [184–186].

### 1.6.2. Pyrolysis oil

Pyrolysis oils are pseudo-homogeneous liquids (from transparent yellow to dark brown color). The pyrolysis oils are obtained by condensation of the pyrolysis vapors, after separation of the char particles. The term pyrolysis oils have several synonyms e.g. pyrolytic liquids or even bio-oils. Pyrolysis oils differ significantly from fossil fuels in terms of both physical properties and chemical composition. *Table 1.8* compares the main properties of plastic sourced pyrolysis oils, bio-oils and conventional diesel.

Costs to produce pyrolysis oil/bio-oil can be considerably different depending on the capacity, the used raw materials, the location (national laws, operating surroundings) or even the optimal product structure. In general, large-scale plant has lower production costs. One of the most difficulties regarding the large scale commercialization of the pyrolysis plants are the product quality [187]. Especially the contaminants and the missing standardization of the products are the most problem which have to be solved, against the economic operation of the plants.

Because they are carbon-neutral, pyrolysis oils have significant potential and advanced environmental impact to substitute fossil sourced hydrocarbons. The process parameters have a key role in the pyrolysis oil composition. The rapid cracking of molecules leads to a mixture of complex chemicals. Moreover, the rapid condensation of hot vapors freezes the unsaturated chains and their storage can cause further problems (e.g. polymerization reactions and increase the yield of high molecular weight compounds). The high oxygen content in the feedstock (biomass or some types of plastic) can cause various undesired compounds such as acids or molecules with carbon-oxygen double bonds that tend to polymerize over time and increase the viscosity of the product [188]. On the other hand, the presence of oxygen in the composition of the oils is the main reason in differences in the properties observed when comparing the pyrolysis oil with a conventional hydrocarbon fuel (*Table 1.8*) [189]. In general, the lower oxygen content of pyrolysis oil can be found at a higher temperature and using longer residence time [190].

**Table 1.8**  
The main properties of different sourced liquids [189]

	<b>Pyrolysis oil</b>	<b>Bio-oils</b>	<b>Diesel fuel</b>
<b>C, %</b>	70-85	48-60	~86
<b>H, %</b>	7-12	5-8	~14
<b>O, %</b>	<5	34-45	-
<b>N, %</b>	<1	<1	-
<b>Na, K, %</b>	<0.1	<0.1	-
<b>Cl, %</b>	<1	<1	-
<b>S, %</b>	<0.1	<0.1	0.9
<b>Density (15°C), g/cm<sup>3</sup></b>	0.790-0.920	0.800-1.300	0.85
<b>LHV, MJ/kg</b>	40-45	13-18	42.9
<b>Viscosity, mm<sup>2</sup>/s (50°C)</b>	1.0-5.0	0.5-80	2.5
<b>Water content, %</b>	-	<35	<0,1
<b>pH</b>	-	2-3.7	-
<b>Cetane number</b>	~50	~30	55
<b>Flash point, °C</b>	~42	~40	50
<b>Solid particles, %</b>	<0.5	<0.5	-
<b>Boiling range, °C</b>	20-360	20-360	20-340

Waste polymers are decomposed via  $\beta$ -scission, therefore the concentration of unsaturated hydrocarbons is relatively high. Typically the waste plastic derived pyrolysis oil contained 20-70% unsaturated hydrocarbons, depending on the raw materials and conditions. The biomass derived bio-oils had less (20-60%) unsaturated hydrocarbons. In

general, catalysts can decrease the amount of unsaturated hydrocarbons. The unsaturated hydrocarbons can easily polymerize led to the formation of larger molecules which can cause a further problem during the application, transportation and storage [191]. One of the another role of the zeolite catalysts led to aromatization reactions, therefore synthetic zeolites (e.g. ZSM-5, Y-zeolite) can increase the aromatic content of the liquid products. The aromatic concentration of pyrolysis products is low using low temperature without catalyst. Pyrolysis product with high aromatic content (30-90%) could be obtained only from raw materials, with aromatic ring in the monomer structure (e.g. PET, PS, ABS, cellulose, etc.) without catalysts. However, the mostly investigated waste fractions resulted considerably less aromatics in pyrolysis/bio oils (10-30%).

The water content in the pyrolysis oils originates from the moisture in the biomass and the product of dehydration reactions during the pyrolysis and depends mostly on operating conditions. The presence of water can decrease the heating value and affect the flashpoint. However, the presence of water makes it possible to reduce the viscosity, which is an advantage for its transport [192–194]. In general, the viscosity of pyrolysis oils and bio-oils is relatively high, which can be decreased not only by water but also by increasing temperature [195,196].

The solid residues in pyrolysis oils are typically less than 0.5%, which is blamed by the kind of raw material (e.g. biomass, plastics containing inorganic filler), process (e.g. fluidized bed), and the efficiency of the solid separation system (e.g. cyclones, etc.). The presence of solid residues in pyrolysis oils can cause erosion and corrosion with engine and valve shutdowns and even its deterioration when the ash content is more than 0.1%. Besides, the presence of alkali metals in ashes (e.g. sodium and potassium) are responsible for the formation of solid deposits and corrosion phenomena [197].

### **1.6.3. Char**

The term “char” refers to the solid residues produced at different stages of the thermochemical process. The pyrolysis char represents up to 35% by weight of the initial raw material depending on its source. The char is carbonaceous material (the carbon content is between 75-85%) that can contain many inorganic and metallic compounds depending on the raw material and the operating conditions. If inorganic and metallic content is high (> 5%), the pyrolysis char can hardly be used as fuel for various technical reasons [37]. *Table 1.9* summarizes the main properties of the waste sourced chars [198]. The char can



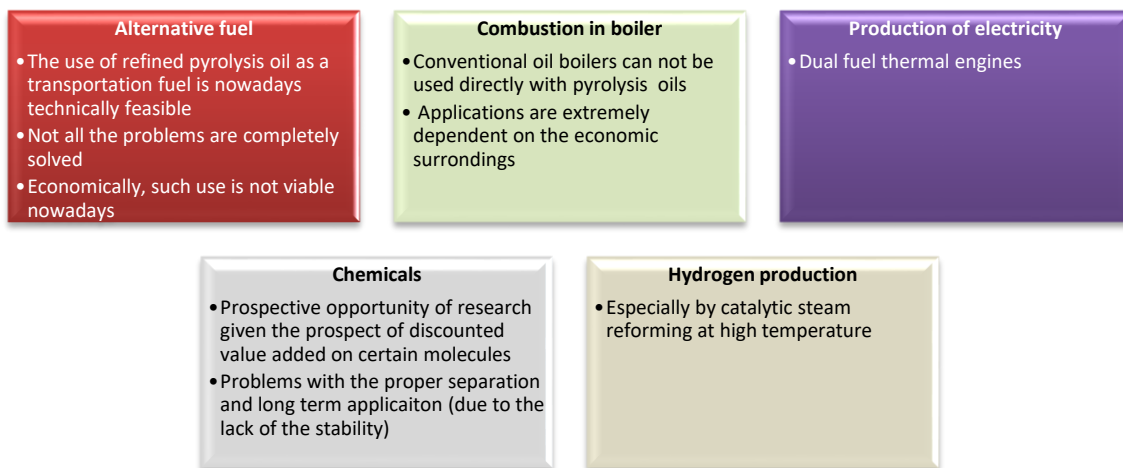
have diverse valorization paths such as combustion for heat and power generation, or even for syngas production by gasification, or use as adsorbents. The concentration of oxygen and hydrogen is lower than carbon because they are more volatile in the form of hydrocarbons, tar vapors, H<sub>2</sub>, CO and CO<sub>2</sub> [199]. The H/C ratio of the char is lower than that of the raw materials because the hydrogen in the form of compounds is accumulated in the gases and pyrolysis oil fractions [200]. The pH of the biomass sourced char is 4-12 [201], and lower value should be obtained at higher temperatures and with less oxygen in the raw material [201,202]. Char is also composed of some of the hydrocarbons that remain from the pyrolysis reactions (heterocyclic compounds, substituted furans, phenols, benzene, carbocyclic groups and aliphatic) [203].

**Table 1.9**  
The main properties of chars [198]

	Plastic sourced	Biomass sourced
<b>C, %</b>	75-85	75-82
<b>H, %</b>	1-3	2-3
<b>O, %</b>	10-15	15-20
<b>N, %</b>	<0.5	<0.5
<b>S, %</b>	<0.05	<0.05
<b>pH</b>	-	4-12
<b>HHV, MJ/Kg</b>	29-32	27-30
<b>BET surface area, m<sup>2</sup>/g</b>	5-20	5-100

### 1.7. Further utilization of pyrolysis oils

The further use of pyrolysis product is one of the most important aspects for their utilization. *Figure 1.8* shows some examples for the pyrolysis oil application. Pyrolysis oils may be a substitute fuel for many applications such as boilers, engines or turbines for power generation. Parallel to this, there is a more or less wide range of organic compounds that can be extracted and entered into the manufacture of chemicals related to the fields of fine chemistry [204–206].

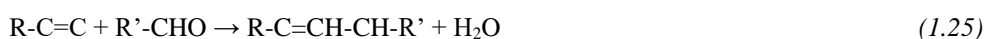


**Figure 1.8**  
Some possibilities for the utilization of waste sourced liquid products

## 1.8. The problem of pyrolysis oil

Depending on the raw materials and reaction conditions, the waste sourced pyrolysis oils should be highly active, causing many changes in their chemical and physical properties during the transportation and storage [207–209]. The aging results phase separation, volatiles evaporation, viscosity and acidity increasing. Oasmaa et al. found that the main changes during aging are the increase in the water-insoluble and the decrease in carbonyl compounds, e.g. ketones and aldehydes. The presence of highly active organic functional groups such as phenols, carboxylic acids, aldehydes, alcohol and unsaturated hydrocarbons can be blamed for the aging reactions [210,211]. It is also known, that the aging of unstable compounds can promote the polymerization reactions, which increases the molecular weight, and the viscosity. The high viscosity oil makes it harder to process and pump. The pyrolysis of materials with high oxygen content (e.g. biomass, paper or PET) resulted different oxygenated compounds with acidic properties, which cause corrosion. The presence of PVC in the feedstock led to chlorinated hydrocarbons. The water content in the pyrolysis oils can cause phase separation, which complicate its pumping. The presence of solid residues in pyrolysis oils can cause erosion [207,212–220]. Some typical reactions during the aging are listed below (1.19-1.26). Kim et al. proved that the low molecular weight components may contribute to the polymerization with pyrolytic lignin that causes the increase of average molecular weight [221]. Others concluded that the presence of free radicals is responsible for the pyrolysis oil instability in the case of stor-

age [210,211]. Pyrolysis oil is highly sensitive to heat and oxygen because some of pyrolysis oil compounds are more reactive in the presence of oxygen and at heat [210,211]. However, the correlation between raw material and viscosity was not found. At low temperatures, biomass-based oils are non-Newtonian fluids [222].



Corrosion is another important property of the waste-derived hydrocarbons. Pyrolysis oil typically contains up to 20% acids, and its acid number is up to 100 mgKOH/g raw material. It has been described that biomass sourced pyrolysis oils are very corrosive and eroding the constructional materials [223]. In general, there is no corrosion problem with the waste LDPE, HDPE, PP or PS sourced pyrolysis oils. Aubin et al. [224] found that the corrosion rate of pyrolysis oil would be boosted with its water content. Boucher et al [209] stated that stainless steel and brass could not be impacted by pyrolysis oil at any temperatures. Darmstadt et al. [225] shown that copper could be slightly rusted by the pyrolysis oil derived from vacuum pyrolysis of woody bark residues, whereas stainless steel was anticorrosive. Furthermore, they investigated the changes in the metal surface to understand the oxidation mechanism. The presence of water in the hydrocarbon fraction can increase the rate of internal corrosion, which is the most costly corrosion problems. Furthermore, high water content in fuel can led to significant increase in the emission of CO and unburned hydrocarbons.

The TAN is widely used to follow the tendency for corrosion. TAN does not effectively indicate corrosiveness in pyrolysis oil since it also measures the non-acidic oxygenated contents, like phenols. It has been established that TAN correlates to total volatile acids [226].

## **1.9. Stability improving of the pyrolysis oil**

In some cases, the waste sourced pyrolysis oil quality limits its application as a transportation fuel. Consequently, the upgrading of pyrolysis oils before its use is indispensable.

### **1.9.1. Pre-situ quality improving**

#### **1.9.1.1. *Physical pre-treatments***

The size and shape of the raw material can affect the heat and mass transfer [227]. The energy requirements of the pyrolysis reactions vary significantly depending on the raw materials (0.5-2 MJ/kg) [228–230]. Smaller biomass and/or plastic particle under high temperatures led to faster reactions, more volatiles and less char [231]. The particle size up to 5 mm exhibited an advantageous effect on the liquid oil yield. Spherical profile raw material has produced the lower volatiles and tar yields than the others shapes [234]. On the other hand, not only the quantity but also the composition of the products can be significantly influenced by pre-treating the raw materials. For example, the impurity content of products can be significantly reduced by cleaning and washing raw materials.

#### **1.9.1.2. *Thermal pre-treatments***

Raw materials (e.g. fresh biomass) should contain moisture (up to 80%) [232]. High moisture content decreases the heating value of the oils and causes long term problems during storage or transportation, therefore the moisture should be reduced right before the pyrolysis.

#### **1.9.1.3. *De-mineralization***

The mineral elements (e.g. K, Cl, S, Ca, Si or Mg) especially found in biomass raw material, because in general plastics are free from minerals. They can catalyze different chemical reactions and cause the secondary transformation of the primary products [233,234] and promote the deterioration of the pyrolysis oil properties, e.g. increasing viscosity and density during storage [235]. One of the effective pretreatment is to reduce the mineral content by washing the biomass with water, alkaline and/or acidic solutions. Washing with dilute acid and hot water led to a slight decomposition of hemicellulose [236]. Washing with dilute alkali disorders the lignin assembly and solubilize the hemicellulose [237].

#### **1.9.1.4. Torrefaction**

Torrefaction is a mild thermal treatment that adjusts the configuration and chemical composition of biomass through removing hemicelluloses [238], drying and moderately decreasing cellulose and lignin [239]. Li et al. [240] defined torrefaction as mild heat treatment of biomass at a temperature range between 200 and 300°C, extending 15–30 minutes. Torrefied biomass contains about 80% of the mass and 90% of the energy of the initial biomass [241]. The chemical reaction during the torrefaction is depending on the raw material particle size, temperature, residence time and operation unit. Biomass torrefaction can produce oils with improved storage stability [232] and low-oxygen-content fuel that is appropriate raw materials for pyrolysis [242].

#### **1.9.1.5. Hydrothermal pre-treatment**

The hydrothermal pre-treatment is a wet torrefaction. The hydrothermal pre-treatment utilize water at a temperature range of 150-260°C [243] to solubilize hemicellulose in aqueous solution, conserving cellulose for the pyrolysis procedure [244]. The water should be as a medium or catalyst in further reactions. Hydrothermal pre-treatment has some advantages comparing to torrefaction, such decreases energy consumption due to its lower temperatures which leads to a reduction of bio-char ash content yield [245]. The use of hydrothermal pre-treatment before the pyrolysis has proved an improvement in pyrolysis oil quality, by the reduction of water existent in pyrolysis oil [246].

#### **1.9.2. In-situ quality improving**

The in-situ pyrolysis process uses a catalyst for improving product yield and quality. Several researchers investigated the application of zeolite catalysts for in-situ quality improvement. Mainly the following reactions should be taken place by in-situ product upgrade during the pyrolysis: saturation reactions (which are promoted e.g. by Ni-containing catalyst), volatile yield improvement (due to the acidic sites of the catalysts) and contaminant reduction (by chemical reaction or adsorption) [247]. It was found that the zeolite structure (acidic zeolite catalysts, proton form  $\beta$ , Y, ZSM-5, and Mordenite) could considerably affect the chemical composition of pyrolysis oils. Catalysts can increase the amount of pyrolysis oil and due to deoxygenation reaction decrease the yield of acids; while increasing the yield of ketones and PAHs [233,234]. More aromatic compounds and less carbohydrates were obtained in oil obtained by thermo-catalytic pyrolysis of biomass and the oil had significantly lower oxygen contents [248].

Based on literature data, it was concluded, that there are very few references to scaled-up experimental results in the field of in-situ quality improvement. There are several possible reasons for this, e.g. the price of the catalysts should be used, their availability, and the lack of information about their long-term behavior, applicability, and regenerability. It is also important to mention that in the absence of standardization of pyrolysis products, the additional cost of in-situ quality improvement can only be enforced in product prices with a very significant property improvement. At the same time, improving the quality of pyrolysis products is a key issue for the long-term sustainable operation of the process, because stricter regulations will only allow products of a certain quality to be sold economically.

### **1.9.3. Post-situ quality improving**

The post-situ catalytic improving pyrolysis vapors also using catalysts. It is important to mention, that generally hydrotreating step is needed to stabilize the pyrolysis oil, which principally increases the process complicity. Furthermore, the hydrogen consumption is also a significant part of the operating costs [249]. ZSM-5 based catalysts, amongst the large diversity of microporous materials, have been most widely studied for their application in catalytic pyrolysis. Owing to its shape selectivity, strong acidity, ion exchange capacity and unique solid acid physical characteristics [233,234].

### **1.9.4. Ex-situ quality improving**

The ex-situ quality improvement uses additives to deteriorate the undesired properties of the pyrolysis oils. Especially the following additives are used: antioxidant, stabilizer, detergent, deactivator, corrosion inhibitor, and biocide [250].

## **1.10. Tests for investigation of the long-term property of the pyrolysis oil**

Pyrolysis oils go through oxidation and polymerization during storage, result in agglomerations, polymerization and intense loss of combustion efficiency. Gloomy oil is symbolic of oxidation, while smoky oil indicates the polymerization of pyrolysis oil. These components fall to the bottom of the tank named sludge [251].

### 1.10.1. Aging tests

The thermal stability of hydrocarbons is well defined as the resistance against elevated temperature. Accelerated thermal aging procedures have been largely approved for thermal stability tests [233,234]. In an accelerated thermal aging testing, the pyrolysis oil is stored at an elevated temperature and the chemical and physical properties before and after the aging procedure are analyzed [252]. An illustration of the accelerated aging in a round-robin study on pyrolysis oil viscosity and stability was pronounced from the International Energy Agency (IEA). In general, the pyrolysis oil sample is heated up at 80°C for 24 hours and then cooled at room temperature for 1.5 hours before analysis. The storage of a pyrolysis oil sample for 1 year at room is equivalent to the aging of the oil 24 h at 80°C [253]. As the aging procedure causes considerable changes in carbonyl products and water-insoluble, the compositional changes in those products are used to estimate the thermal stability of pyrolysis oil [254]. **Table 1.10** summarizes the different stability tests for pyrolysis oil characterization.

**Table 1.10**  
The different used stability test methods to assess the pyrolysis oil stability

Stability test method	Accelerated /Non-accelerated aging reaction parameters	Ref
Viscosity change	at 40, 50 and 80°C for up to 168 h/at room temperature for up to one year	[209]
	for 24 h at 80 °C/ten days at room temperature	[261]
	at 60 °C for 4 days/ 6 hours of aging at 90 °C/ 3 months at room temperature	[262]
	at 80 °C for 16 h	[263]
	at 80 °C for 1, 3, and 7 days	[264]
	at 90 °C for 8, 16, 24 h	[253]
	at 85 °C for 7 days/ at room temperature for 5 months	[265]
	at 80 °C for 180 h	[266]
	at room temperature for 12 months	[267]
	at room temperature for 270 days.	[268]
Average molecular weight change	for 1 week at 80 °C/1 year at room temperature	[269]
	at 80 °C for 24 h / 110 °C for 24 h	[270]
	at 80 °C for 16 h	[263]
Water content change	at 80 °C for 1, 3, and 7 days	[264]
	at room temperature for 12 months	[267]
	at 80 °C for 24 h / 110 °C for 24 h	[270]
	at 80 °C for 16 h	[263]
Carbonyl content change	at room temperature for 12 months	[267]
	at 80 °C for 24 h / 110 °C for 24 h	[270]
	at 80 °C for 16 h	[263]
Solid deposition	at room temperature for 1 day, 30 days, and 60 days	[271]

As an alternative to measuring those variations directly, correlations have been established between those compositional changes and quantifiable parameters. For example, the increase in water-insoluble [252] can be correlated with the rise in the average molecular weight and the rise in the viscosity of the wood pyrolysis oil. Pyrolysis oil viscosity is a significant parameter to evaluate its quality and practical application. The change in viscosity of pyrolysis oil is commonly linked with the rise in molecular weight caused by the polymerization reactions that progress in the pyrolysis oil [255].

The key reason for the rise in molecular weight is the condensation and polymerization reactions of low molecular weight constituents for the duration of storage [252,256].

On the other hand, ketones and aldehydes are considered as the major contributors to the pyrolysis oil instability for the duration of storage. Owing to their high reactivity, esterification, aldol condensation, acetalization and supplementary reactions that result in the development of polymers or dimers that take place in the water-soluble fractions of pyrolysis oil. Furthermore, aldehydes could react with pyrolytic lignin in the water-insoluble fraction via phenol-formaldehyde condensation [207].

The solid deposit content in pyrolysis oil is generally less than 1%. These solids is made up of partly separated coke formed during pyrolysis reaction, impurities in the feedstock (e.g. dust), and impurities got in the case of collection and storage. Common heavy oil boilers have no severe requirements for solid content; consequently, pyrolysis oil can be used for this application easily. Conversely, the high standard requirements of diesel injection systems can turn out to be damaged by the particulates in pyrolysis oil, so the use of pyrolysis oil in this application is limited. The solid content in pyrolysis oil should be reduced as those particulates can also perform as catalysts to accelerate the aging procedure [257,268].

The main source of water in pyrolysis oil is from free water in the raw materials and the dehydration reaction in the case of pyrolysis. However, in the case of pyrolysis oil storage, aging reactions also produce water. Commonly, phase separation arises while the water content in pyrolysis oil is higher than 30%. As pyrolysis oil contains various organic substances with low molecular weights, the customary drying technique is not suitable for assessing water content [220,259,260].

Oxidative stability is the ability of pyrolysis oil to withstand the effect of atmospheric oxygen and to preserve the natural properties of pyrolysis oil. Organic matters and oxygen



in pyrolysis oil tend to form super-oxides. Super-oxides can accelerate the polymerization of other substances such that the polarity differences within pyrolysis oil substituents are boosted [220]. Hilten et al. concluded that the initial oxidizing temperature and oxidative stability of pine pyrolysis oil were both greater than those of peanut shells pyrolysis oil [219]. The authors also found that the addition of organic solvents not just reduced particulate matter deposition, but also support the oxidative stability of pyrolysis oil. Garcìa-Pèrez et al. examined the oxidative stability of emulsified oil (biodiesel/pyrolysis oil). The results indicated that the initial oxidizing temperature of the biodiesel/pyrolysis oil increased when more pyrolysis oil was emulsified [132].

### **1.10.2. Corrosion tests**

Pyrolysis oils obtained from plastic and/or biomass have organic compounds and acids that can be destructive to metal-based structures used for storage tanks and pipelines. Many corrosive constituents were identified in the pyrolysis oil such as water, formic acid, catechol, lacto bionic acid, etc. In a prior investigation, formic acid in pyrolysis oils was indicated as responsible for corrosion. Stainless steels could offer appropriate corrosion resistance in pyrolysis oils. Nevertheless, it is also claimed that pyrolysis oils at 50°C caused erosion for 409 stainless steel, but not in 316 L and 304 L austenitic stainless plates of steel, demonstrating that not all stainless steels are resistant to corrosion in pyrolysis oils [272,273].

Pyrolysis oil produced from rice-husk has been presented significant erosion to mild steel, even at room temperature. Lu et al. indicated that the corrosion rates of aluminum alloys were lower compared to mild steel, and brass was established to be comparatively resistant to the general corrosion at room temperature [274]. Aubin and Roy examined the effect of water content, temperature and formic/acetic acid concentration on the corrosivity of pyrolysis oils to dissimilar alloys. Pyrolysis oils were indicated not to be very corroding to the cast iron under ambient temperature when tested in pyrolysis oils with low water content for all concentrations of acids. On the other hand, increasing the examination temperature to 45°C, the iron erosion radically increased. Aubin et al. also established that the corrosion rate of pyrolysis oil became higher with the increase of water content [224].

Previous investigations on oak and pine pyrolysis oils have revealed that carbon steel, 516-Gr70, undertakes significant corrosion. Despite the oak pyrolysis oil in this investigation had lower water content; it showed higher corrosiveness than the pine pyrolysis oils. Darmstadt et al. verified the corrosiveness of softwood bark pyrolysis oil with a substantial amount of water, made by vacuum pyrolysis reactor, at 80°C and showed that the aluminum alloys corroded to a smaller degree, copper was significantly corroded by the pyrolysis oil, however, 316 stainless steel was not affected [228]. Keiser et al. found significant erosion of 2¼ Cr-1 Mo steel and carbon steel for pyrolysis oils at 50°C [275].

Several alloys were tested by Singh et al using pine based pyrolysis oil. The top film of pyrolysis oil was a light-brown layer with high water content (~69% water) comparing to the bottom layer, which was more viscous and dark-brown in colour (~19% water). Carbon steel corrosion behavior exhibited major differences when tested in each separated layer. At 50 °C the corrosion rate of carbon steel was nearly 75 mpy in the light-brown oil however only almost 14 mpy in the dark-brown oil. Stainless steels samples had less corrosion rate compared to brass and copper samples which were tested in pine pyrolysis oil. Corrosion rates for copper and brass were pointedly lower than the carbon steel and aluminum samples under the same condition [212].

### **1.11. Main conclusion and critical evaluation of available literature**

Based on the literature data, it was concluded, that pyrolysis is a promising alternative for recycling of polymer waste. Using the pyrolysis process, polymer waste can be converted into liquid products, solid residues (char) and gases at high temperature. Non-catalytic pyrolysis requires a high temperature and reaction time, and the liquid products from thermal pyrolysis are distributed over a wide range of carbon numbers, which requires treatment to improve their qualities. As an alternative, catalytic pyrolysis offers the potential to solve these problems. The use of an appropriate catalyst adjusts product yield and component distribution and significantly reduces pyrolysis temperatures and reaction time, resulting in a more cost effective process with higher value products.

Polyethylene and polypropylene are the two main constituents of plastic waste materials that are found in municipal waste. As has been demonstrated in the literature, the use of catalysts in the waste polymer degradation is necessary to address efficient, high quality conversion and selectivity in products. Therefore, one of the objectives is to study the effect of catalysts on the degradation of polymers waste.

In general, the level of activity of the catalyst in the pyrolysis of polymers increases with the increasing number of acid sites. Therefore, zeolite-based catalysts achieve a higher conversion than non-zeolite catalysts. A high conversions and attractive product distributions are obtained over zeolites catalysts, leading to high yields in terms of gaseous products.

From a different perspective, pyrolysis oils are highly unstable and self-reactive mixtures, which explains the main problem of their poor storage stability. The chemical composition tends to change over time due to reactions between the components by polymerization, condensation, esterification, and etherification. Reflecting an increase in viscosity and density. This process, called “aging”, is catalyzed by the presence of char particles and by high temperatures. Chemical reactions cause a change in polarity favoring phase separation, which greatly limit the use of oils.

Based on the literature overview, due to many of unsolved problems, the stability improvement of waste derived pyrolysis oil looks attractive area for further investigation. One of the biggest challenge is the application of catalyst to increase the yields of volatiles and improve their quality in one step by in-situ scaled up process. Furthermore, the comparison of different scaled up processes for in-situ quality improving is also looks attractive research area.

## **2. EXPERIMENTAL PART**

Based on the literature review, it is clear that there are relatively few information about the real application and testing of hydrocarbon fractions obtained by the cracking polymer waste. Of these, most focus on energy recovery and only few researches have focused on the long-term storage, transport, and stability characteristics of pyrolysis oil. The main objective of my thesis was to produce liquid hydrocarbons in different reactor systems using real waste. Then the longer-term stability of the fraction was investigated. Catalysts were used to increase the amount of volatile fractions and favourably modify the composition of hydrocarbon fractions. Comparing the results obtained in this way, the effect of different feedstocks, catalysts and reactor systems was investigated and concluded. The raw materials were real wastes. Plastic waste was chosen because their recycling is unsolved problem especially in their contaminated form. The chlorine contamination can cause a serious problem during recycling. On the other hand in the form of wastes, the plastics are mixed with other constitutes, e.g. paper and biomass. Therefore, the effect of the paper and biomass presence was also investigated. The stability of the pyrolysis oil was tested at 80°C for 7 days and their main characteristics were determined at certain intervals. In addition to pyrolysis oil, the composition and main characteristics of the gas and heavy oil products was also followed.

### **2.1. Raw materials**

#### **2.1.1. Waste plastic, biomass and paper**

Three different kinds of real wastes were used as raw materials: chlorinated polyolefin rich plastic waste, plastic waste containing biomass and plastic waste containing paper. Each particle of the representative amount (100g of each) of raw materials was weighed. The paper, biomass and plastic particles were separated and the biomass-plastic or paper-plastic ratio was determined in case of plastic waste containing biomass and plastic waste containing paper, respectively. The composition of plastic constituents of raw material was identified by FTIR method (Bruker Tensor 27 instrument) based on spectrum comparison. Raw materials had been cut and crushed by a laboratory miller (Dipre GRS 183A9 type). The appearance of the crashed raw materials is shown in *Figure 2.1*.



**Figure 2.1**  
The composition and appearance of the used raw materials

The compositions of the raw materials are shown in **Table 2.1**. Regarding the chlorinated waste plastics, it consisted of 35% LDPE, 32% HDPE, 24% PP, 4% PVC, 3% ethylene-propylene dimer and 2% PS. The waste plastics containing biomass has 24 % LDPE, 22 % HDPE, 16 % PP, 35 % biomass and 3 % of non-defined material. Furthermore, the waste plastics containing paper has the following composition: 24% LDPE, 21% HDPE, 17% PP, 17.5% newspaper, 17.5% cardboard waste and 3% other or non-defined materials.

**Table 2.1**  
The composition of raw materials

	<b>Chlorinated waste plastics</b>	<b>Plastic waste containing biomass</b>	<b>Plastic waste containing paper</b>
<b>LDPE</b>	35%	24%	24%
<b>HDPE</b>	32%	22%	21%
<b>PP</b>	24%	16%	17%
<b>PVC</b>	4%	-	-
<b>Paper</b>	-	-	17.5% newspaper, 17.5% cardboard
<b>Biomass</b>		35%	
<b>Other/Non-defined</b>	5%	3%	3%

### 2.1.2. Raw materials for comparative study of different aging tests

The tested pyrolysis oils were derived from real polymer wastes (100% HDPE, 100% PP, 100% PS, MPW (25% HDPE; 25% LDPE; 30% PP; 10% PS and 10% PET) and MSW (10% HDPE; 10% LDPE; 20% PP, 5% PS, 5% PET, 25% paper and 25% biomass)). The main properties of the raw materials are summarized in **Table 2.2**.

**Table 2.2**  
The main properties of different raw materials

	<b>HDPE</b>	<b>PP</b>	<b>PS</b>	<b>MPW</b>	<b>MSW</b>
<b>Source</b>	waste HDPE (from municipal waste)	waste PP (from packaging and municipal waste)	waste PS (from municipal waste)	municipal plastic waste	municipal solid waste
<b>Ultimate analysis</b>					
<b>C</b>	81.5	84.1	89.8	80.3	72.1
<b>H</b>	18.5	15.9	10.2	12.9	8.1
<b>N</b>	-	-	-	-	0.6
<b>O</b>	-	-	-	6.8	20.2
<b>Moisture, %</b>	0.8	0.9	0.5	1.7	5.1
<b>Ash, %</b>	0.9	1.5	0.8	5.3	19.2
<b>HHV, MJ/kg</b>	43.9	41.8	38.9	39.8	22.7

## 2.2. Catalysts

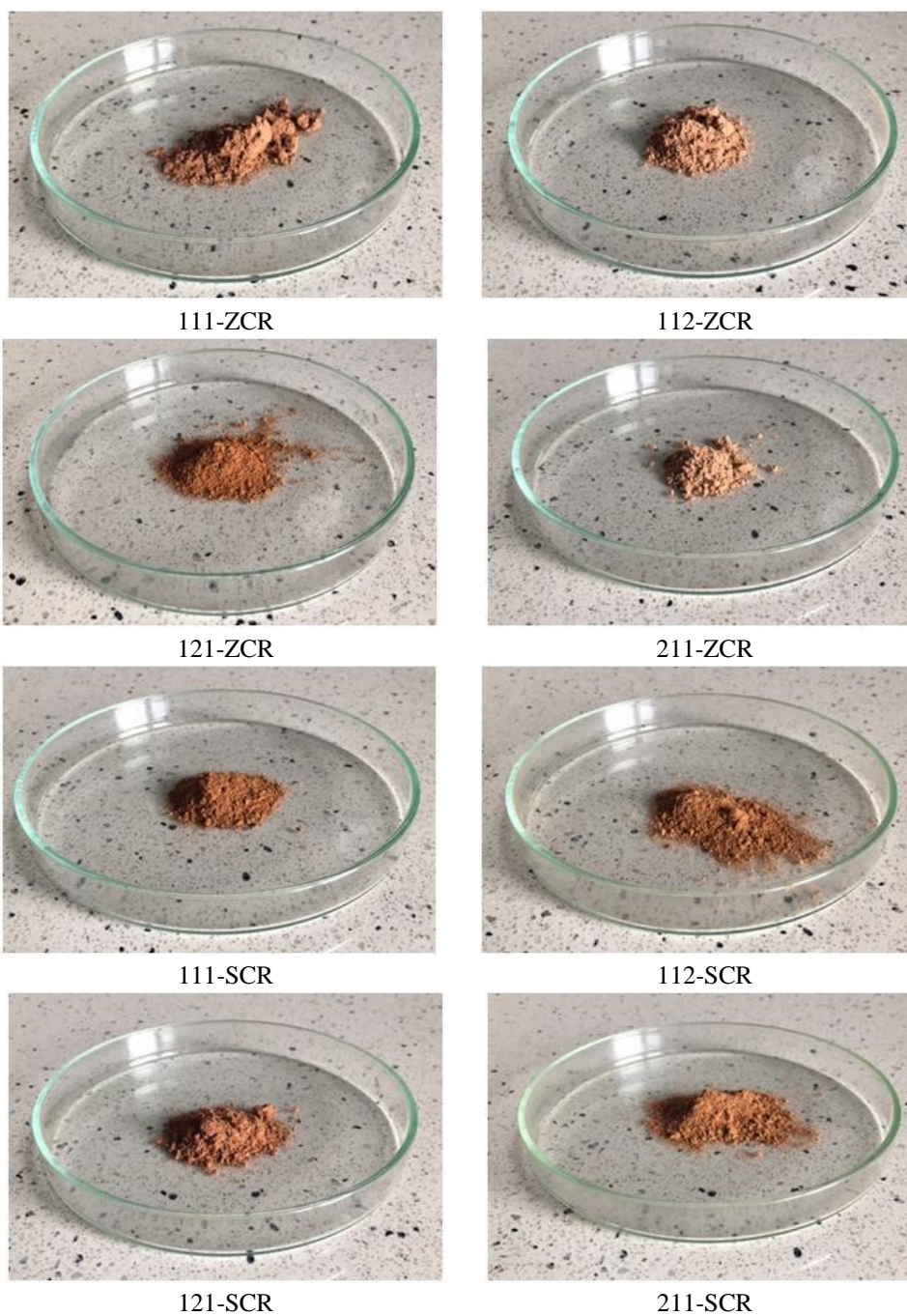
Mixtures of different modified synthetic zeolite (Ni/ZSM-5 and Ni/SAPO-11) catalysts,  $\text{Ca(OH)}_2$  and red mud (composed mainly of iron oxide that is generated in the industrial production of alumina) were used to enhance the waste polymer decomposition and modify the product properties and enhance the long term application [276,277].

The ZSM-5 ( $[\text{Na}_n(\text{H}_2\text{O})_{16}][\text{Al}_n\text{Si}_{96-n}\text{O}_{192}]$ ) catalyst supporter is MFI-type 10 membered ring channel synthetic zeolite with  $5.3 \times 5.6 \text{ \AA}$  channels, while AEL-type, crystalline silicoaluminophosphate (SAPO-11) catalyst ( $[\text{Na}_n][\text{Al}_{20}\text{Si}_n\text{P}_{20-n}\text{O}_{80}]$ ) supporter is a one-dimensional but also 10-membered, with elliptical pore channel synthetic zeolite with  $6.3 \times 3.9 \text{ \AA}$  pore size [276,277]. The before listed catalysts were used in their mixture according to *Table 2.3*.

**Table 2.3**  
The composition of the catalysts, % [276,277]

	<b>Ni/ZSM-5</b>	<b>Ni/SAPO-11</b>	<b>Ca(OH)<sub>2</sub></b>	<b>Red mud</b>
<b>111-ZCR</b>	33.33	0.0	33.33	33.33
<b>112-ZCR</b>	50.0	0.0	25.0	25.0
<b>121-ZCR</b>	25.0	0.0	25.0	50.0
<b>211-ZCR</b>	25.0	0.0	50.0	25.0
<b>111-SCR</b>	0.0	33.3	33.3	33.3
<b>112-SCR</b>	0.0	50.0	25.0	25.0
<b>121-SCR</b>	0.0	25.0	25.0	50.0
<b>211-SCR</b>	0.0	25.0	50.0	25.0

Catalysts signed with 112 have high synthetic zeolite content, while 121 and 211 marked catalyst mixtures have high red mud and  $\text{Ca}(\text{OH})_2$  content, respectively. The elemental constituents (zeolite,  $\text{Ca}(\text{OH})_2$  and red mud) of catalysts were mixed by vibrating ball mixer. The appearance of the catalyst is shown in **Figure 2.2**. Catalysts mixtures have similar appearance, however due to the high percentage of the red mud, 121-ZCR and 121-SCR marked catalyst mixture had a little more red in colour.



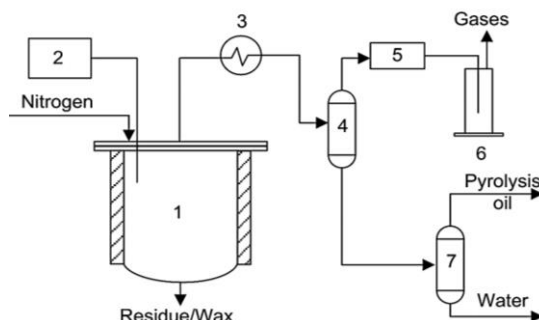
**Figure 2.2**  
The appearance of the catalysts

## 2.3. Processes for pyrolysis

Two different processes were used during the experimental work to investigate the thermal and thermo-catalytic decomposition of wastes: a laboratory-scale batch and a laboratory-scale continuous reactor.

### 2.3.1. Batch process

In the case of the batch pyrolysis, raw materials were decomposed in a stainless steel laboratory-scale reactor at 500-550°C temperature. For inert atmosphere nitrogen was used with 5 dm<sup>3</sup>/h flow rate (**Figure 2.3**). The reactor was equipped with an electric heating mantle and the set temperature was controlled by PID controller. Before the experiment, a given amount of raw material (50g) and catalyst (2.5g) had been placed into the reactor, then the reactor was assembled and the temperature was elevated by the constant heating rate (25°C/min) to the set value [276]. The produced volatiles from the molten and decomposed raw material had been passed through a water-cooled tubular heat exchanger, where the condensable were transformed into a liquid product. The product yields were calculated based on the mass balance.



**Figure 2.3**

Laboratory scale batch reactor [276]

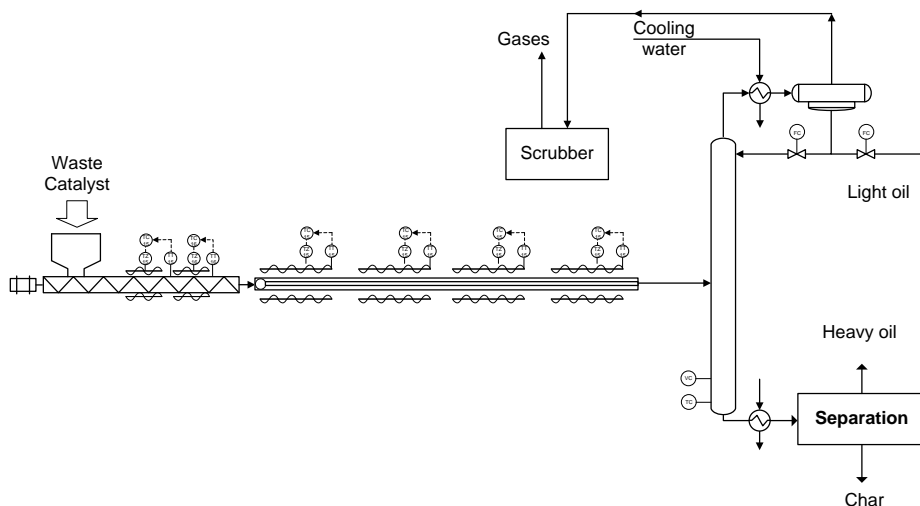
1-reactor, 2-PID controller, 3-heat exchanger, 4-gas/liquid separator, 5-gas flow meter, 6-scrubber, 7-oil/water separator

The hydrocarbon fractions from the reactor were separated into a light oil and hydrocarbon gases in a phase separator. Gases were driven through a gas flow meter then a scrubber filled with 1M NaOH dissolution to catch the chlorinated compounds in case of pyrolysis of chlorinated waste plastics. The condensed fraction was further separated into water and pyrolysis oil in case of plastic containing biomass or paper decomposition.



### 2.3.2. Continuous process

For the decomposition of more raw material, a tubular horizontal bench-scale reactor was used (*Figure 2.4*). The process has three main parts: feeding unit, reactor and separation unit. The feed rate was 750 g hourly. The raw material and catalysts had been mixed manually before they were fed into the reactor. Then the raw materials were pyrolyzed at 550-560°C and the mixtures of decomposed hydrocarbons were separated by atmospheric distillation and hot press filtration (in dedicated cases).



*Figure 2.4*  
The bench-scale horizontal tubular reactor [277]

The distillation column was packed with Raschig ring to accomplish an improved separation rate of light and heavy oils. Regarding the catalytic pyrolysis, 5% of the catalyst was added to the raw material. The bottom product (heavy oil and char) from the distillation column was filtered using high pressure (1.5 barg) and temperature (170°C). The product yields were calculated based on the mass balance [277].

## 2.4. Analytical methods

### 2.4.1. Raw materials

The composition of plastic constituents of raw material was identified Bruker Tensor 27 FTIR instrument using OPUS 5.5 software [276,277].

The elemental composition of raw materials was investigated by Carlo Erba 110 instrument [276,277].

The thermal decomposition of 200mg of raw materials was analyzed by MOM DERIVATOGRAPH Q-1500 D type instrument to obtain more information about the decomposition of raw materials. The heating rate was 20°C/min, while the nitrogen flow rate 40 ml/min [276,277].

#### **2.4.2. Catalysts**

The morphology of catalysts was analysed by N<sub>2</sub> adsorption/desorption isotherms using Micromeritics ASAP 2000-type instrument (ASAP 2000 operational program V1.03). Surface areas were determined by the BET (Brunauer-Emmett-Teller) method from the nitrogen adsorption isotherm and calculated from the nitrogen desorption isotherms using the BJH (Barret–Joyner–Halenda) model [276,277].

The average grain size was investigated by Fritsch Analysette 22 instrument based on Fraunhofer theory [276,277].

The composition of catalysts and red mud was analysed by x-ray method (FEI Thermo Fisher Apreo S LoVac 118 instrument, EDAX AMETEK Octane Elect Plus). Same instrument was used for SEM analysis [276,277].

#### **2.4.3. Gases**

A DANI type GC-FID instrument was used for the analysis of gases hydrocarbon composition: Rtx PONA column (100 m × 0.25 mm, the surface thickness of 0.5 mm) as well as Rtx-5 PONA (100 m × 0.25 mm, the surface thickness of 1 mm). T=30°C isotherm condition was used for sample analyses. The temperature of the detector and injector was 240°C [276,277].

The hydrogen, CO and CO<sub>2</sub> content of the gas products was evaluated by a GC-TCD (Shimadzu GC-2010 gas chromatograph (Carboxen™ 1006 PLOT column (30 m × 0.53 mm)) instrument. The temperature was increased from 35°C (hold time 2 min) to 250°C at 40°C/min heating rate, then the final temperature was maintained until 5 min [276,277].

#### **2.4.4. Light oil**

The liquid products were examined by DANI type GC-FID (Rtx 1 dimetil-polysiloxan capillary (30 m × 0.53 mm, thickens of 0.25 mm)) with the following parameters: 40°C for 5 min, then the temperature was raised by 10°C/min until 350°C and it was

kept at 350°C until 20 min. The detector and injector temperature was 350°C. Constituents were detected in accordance with their retention time, while the pyrolysis oil constitution was assessed by the use of peak areas that belong to the constituents [276,277].

X-ray instrument (PHILIPS MiniPal PW 4025/02 non-polarized EDXRF) was used for the determination of the chlorine content. The spectrometer was controlled by PW 4051 MiniPal/MiniMate Software V 2.0A, fitted out with a rhodium-side window tube anode, Si-PIN detector and beryllium window. The analysis was accomplished in the helium medium [276,277].

The yield of poly-aromatics and mono-aromatics was followed by a HPLC instrument in accordance with EN 12916 standards using HPLC grade n-heptane effluent. The Shimadzu Prominence instrument was fitted with a Refractive Index Detector. The column was tempered to 30°C; the flow was isocratic with 1.0 ml/min. The acquisition time was 15 minutes [276,277].

#### **2.4.5. Aging tests**

An accelerated aging test was performed to follow the long-term application of the pyrolysis oils. Samples were kept in a sample holder at 80°C for 7 days [276,277].

The viscosity (EN 16896), density (EN ISO 12185), and Total Acid Number (TAN) (ISO 6618) were measured at 0, 1, 3, 5 and 7 days of the test at 25°C [276,277].

The oligomers and polymers formed by the aging test were separated from the pyrolysis oil by filtration using VWR (514-0066) filter, Nylon, 0.2 µm, D 25 µm type device. Then the amount of the separated fraction had been weighted and the polymerized ratio was calculated as following (2.1):

$$PR = \frac{m_i - m_o}{m_o} \times 100 \quad (2.1)$$

where  $m_i$  is the weight of the separated oligomers-polymers  $i = 1,3,5,7$  days and  $m_o$  is the weight of the tested sample [276,277].

#### **2.4.6. Corrosion tests**

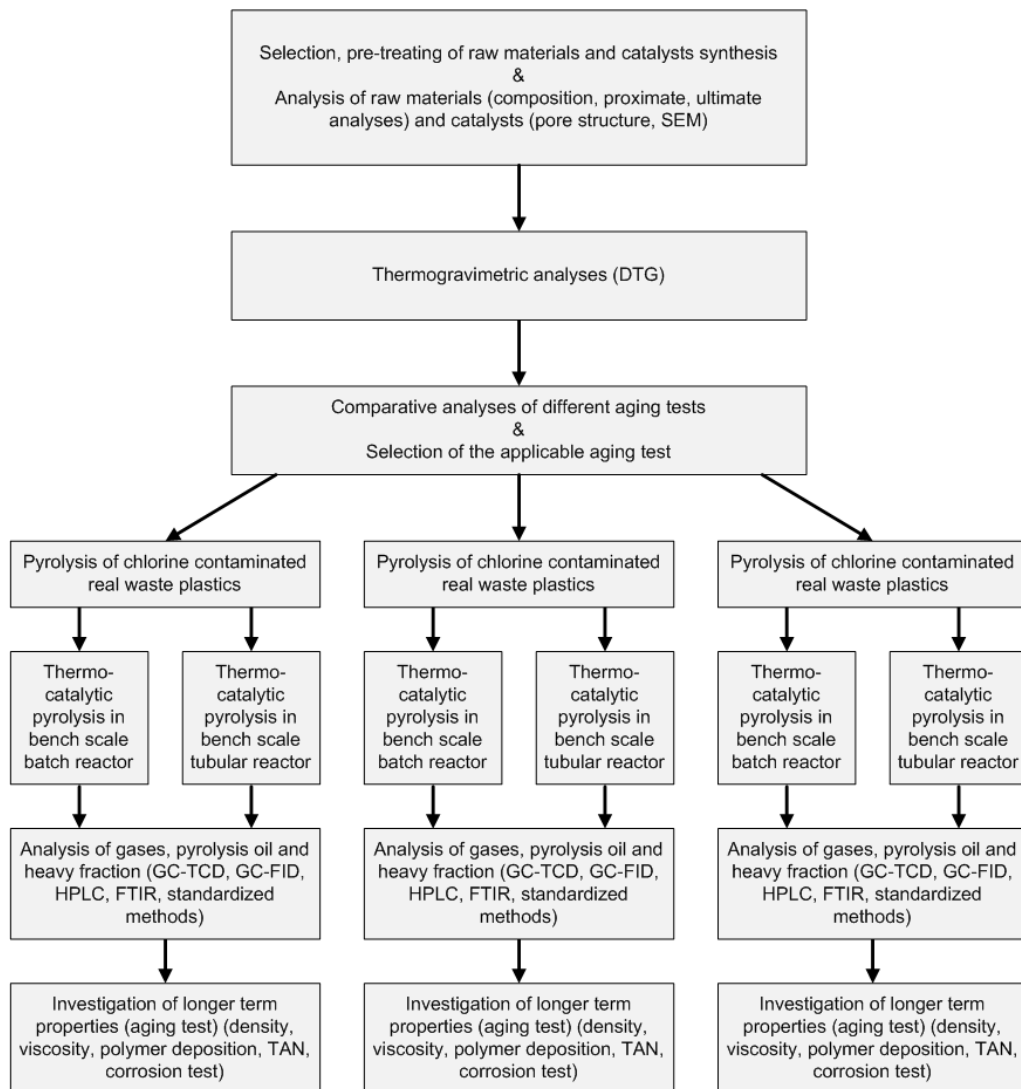
To examine the corrosion property, a copper plate was deposited in pyrolysis oil at 25°C for 60 days and the weight loss of the copper plate was calculated by the following equation (2.2):

$$weight\ loss = \frac{\frac{m_i - m_f}{m_i} \cdot 100}{A} \quad (2.2)$$

where  $m_i$  and  $m_f$  are the initial and final weights of the metal plate,  $A$  is the surface area of the plate [276,277].

## 2.5. Research plan

The research plan is summarized in **Figure 2.5**. During the experimental work, firstly the raw materials had been investigated, then the catalysts were prepared. Then the main characteristics of the catalysts were determined.



**Figure 2.5**  
Research plan

At the beginning of the experimental work different aging tests had been performed and then the results obtained using them were compared. Pyrolysis reactions were taken in batch and tubular reactors to obtain liquid products, then products were investigated and the longer-term utilization of pyrolysis oils was followed by corrosion and aging tests. Then the results obtained by the two different reactor configuration were compared and discussed in case of each raw material. The main reaction parameters are summarized in *Table 2.4*.

**Table 2.4**  
The main reaction parameters for the pyrolysis

Sample number	Raw material	Catalyst	Raw material amount	Catalyst concentration	Process	Temperature
C-1	HDPE	-	250g	-	Batch	550°C
C-2	PP	-	250g	-	Batch	550°C
C-3	PS	-	250g	-	Batch	550°C
C-4	MPW	-	250g	-	Batch	550°C
C-5	MSW	-	250g	-	Batch	550°C
ST-1	Chlorinated waste plastics	<b>111-ZCR</b>	50g	5	Batch	500-550°C
ST-2	Chlorinated waste plastics	<b>112-ZCR</b>	50g	5	Batch	500-550°C
ST-3	Chlorinated waste plastics	<b>121-ZCR</b>	50g	5	Batch	500-550°C
ST-4	Chlorinated waste plastics	<b>211-ZCR</b>	50g	5	Batch	500-550°C
ST-5	Chlorinated waste plastics	<b>111-SCR</b>	50g	5	Batch	500-550°C
ST-6	Chlorinated waste plastics	<b>112-SCR</b>	50g	5	Batch	500-550°C
ST-7	Chlorinated waste plastics	<b>121-SCR</b>	50g	5	Batch	500-550°C
ST-8	Chlorinated waste plastics	<b>211-SCR</b>	50g	5	Batch	500-550°C
ST-9	Chlorinated waste plastics	<b>111-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-10	Chlorinated waste plastics	<b>112-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-11	Chlorinated waste plastics	<b>121-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-12	Chlorinated waste plastics	<b>211-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-13	Chlorinated waste plastics	<b>111-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-14	Chlorinated waste plastics	<b>112-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-15	Chlorinated waste plastics	<b>121-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-16	Chlorinated waste plastics	<b>211-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-17	Plastic waste containing biomass	<b>111-ZCR</b>	50g	5	Batch	500-550°C
ST-18	Plastic waste containing biomass	<b>112-ZCR</b>	50g	5	Batch	500-550°C
ST-19	Plastic waste containing biomass	<b>121-ZCR</b>	50g	5	Batch	500-550°C
ST-20	Plastic waste containing biomass	<b>211-ZCR</b>	50g	5	Batch	500-550°C
ST-21	Plastic waste containing biomass	<b>111-SCR</b>	50g	5	Batch	500-550°C
ST-22	Plastic waste containing biomass	<b>112-SCR</b>	50g	5	Batch	500-550°C
ST-23	Plastic waste containing biomass	<b>121-SCR</b>	50g	5	Batch	500-550°C
ST-24	Plastic waste containing biomass	<b>211-SCR</b>	50g	5	Batch	500-550°C

**Table 2.4**  
The main reaction parameters for the pyrolysis (cont.)

Sample number	Raw material	Catalyst	Raw material amount	Catalyst concentration	Process	Temperature
ST-25	Plastic waste containing biomass	<b>111-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-26	Plastic waste containing biomass	<b>112-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-27	Plastic waste containing biomass	<b>121-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-28	Plastic waste containing biomass	<b>211-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-29	Plastic waste containing biomass	<b>111-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-30	Plastic waste containing biomass	<b>112-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-31	Plastic waste containing biomass	<b>121-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-32	Plastic waste containing biomass	<b>211-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-33	Plastic waste containing paper	<b>111-ZCR</b>	50g	5	Batch	500-550°C
ST-34	Plastic waste containing paper	<b>112-ZCR</b>	50g	5	Batch	500-550°C
ST-35	Plastic waste containing paper	<b>121-ZCR</b>	50g	5	Batch	500-550°C
ST-36	Plastic waste containing paper	<b>211-ZCR</b>	50g	5	Batch	500-550°C
ST-37	Plastic waste containing paper	<b>111-SCR</b>	50g	5	Batch	500-550°C
ST-38	Plastic waste containing paper	<b>112-SCR</b>	50g	5	Batch	500-550°C
ST-39	Plastic waste containing paper	<b>121-SCR</b>	50g	5	Batch	500-550°C
ST-40	Plastic waste containing paper	<b>211-SCR</b>	50g	5	Batch	500-550°C
ST-41	Plastic waste containing paper	<b>111-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-42	Plastic waste containing paper	<b>112-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-43	Plastic waste containing paper	<b>121-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-44	Plastic waste containing paper	<b>211-ZCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-45	Plastic waste containing paper	<b>111-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-46	Plastic waste containing paper	<b>112-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-47	Plastic waste containing paper	<b>121-SCR</b>	0.75kg/h	5	Tubular	550-560°C
ST-48	Plastic waste containing paper	<b>211-SCR</b>	0.75kg/h	5	Tubular	550-560°C

### 3. RESULTS AND DISCUSSION

#### 3.1. Analysis of raw material and catalysts

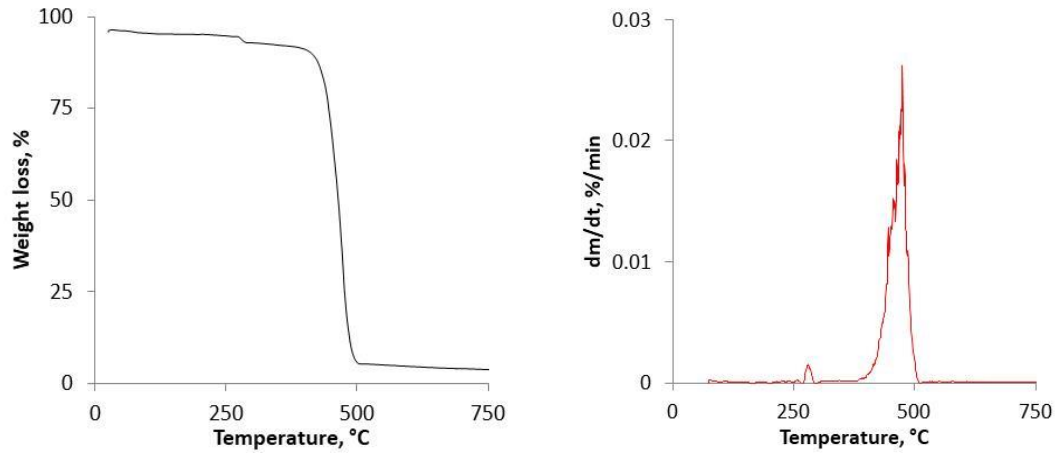
##### 3.1.1. Raw materials

The result of the ultimate and proximate analyses are summarized in *Table 3.1*. Chlorinated waste plastic raw material had the highest carbon and hydrogen content and it contained 1.5% chlorine, while the ash content of it was 4.7%. Both the plastic waste containing biomass and plastic waste containing paper raw materials had oxygen, which was attributed to the cellulose content of paper and biomass (15.5 and 17.5%). Therefore, those raw materials contained less carbon and hydrogen, however, they have more ash (14.8 and 17.4%) and higher moisture content (7.9 and 5.1%).

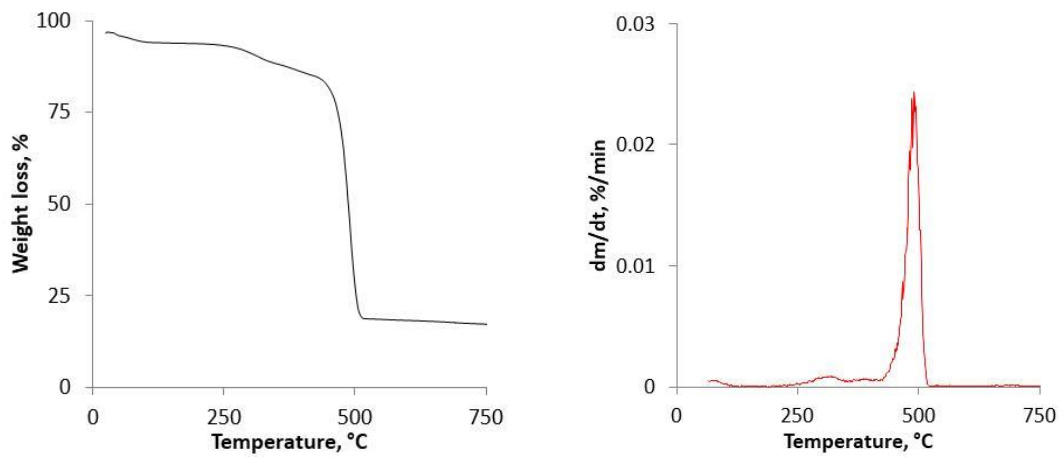
**Table 3.1**  
The main properties of different sourced pyrolysis oils

	Chlorinated waste plastics	Plastic waste containing biomass	Plastic waste containing paper
<b>Ultimate analysis</b>			
<b>C, %</b>	83.2	70.6	69.1
<b>H, %</b>	15.3	12.9	12.4
<b>O, %</b>	-	15.5	17.5
<b>Cl, %</b>	1.5	-	-
<b>Moisture, %</b>	2.5	7.9	5.1
<b>Ash, %</b>	4.7	14.8	17.4
<b>HHV, MJ/kg</b>	42.6	28.9	30.8

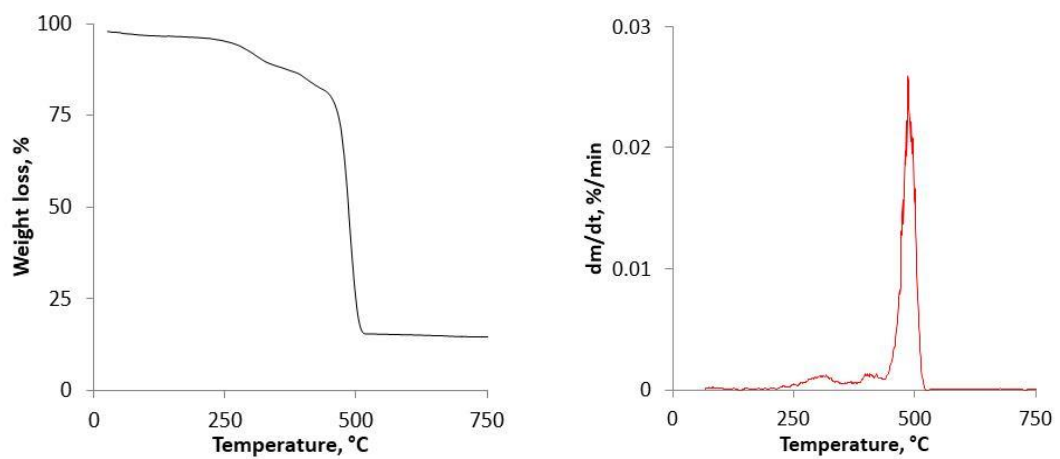
The change in the sample weight and „dm/dt” is summarized in *Figures 3.1-3.3*. Results well demonstrate, that the decomposition of chlorinated plastic waste follows two steps apparent reaction scheme, while that of was a multi steps process in the case of both plastics containing biomass and plastic containing paper. The small peak around 273-298°C can be attributed to the PVC decomposition, while the polyolefin particles of the chlorinated plastic waste decomposed in the temperature range of 398-515°C with a maximum of 473°C. The water content of the sample left the sample crucible up to 150°C in the case of all three samples.



**Figure 3.1**  
Weight loss and “dx/dt” result of chlorinated waste plastic



**Figure 3.2**  
Weight loss and “dx/dt” result of plastic waste containing biomass



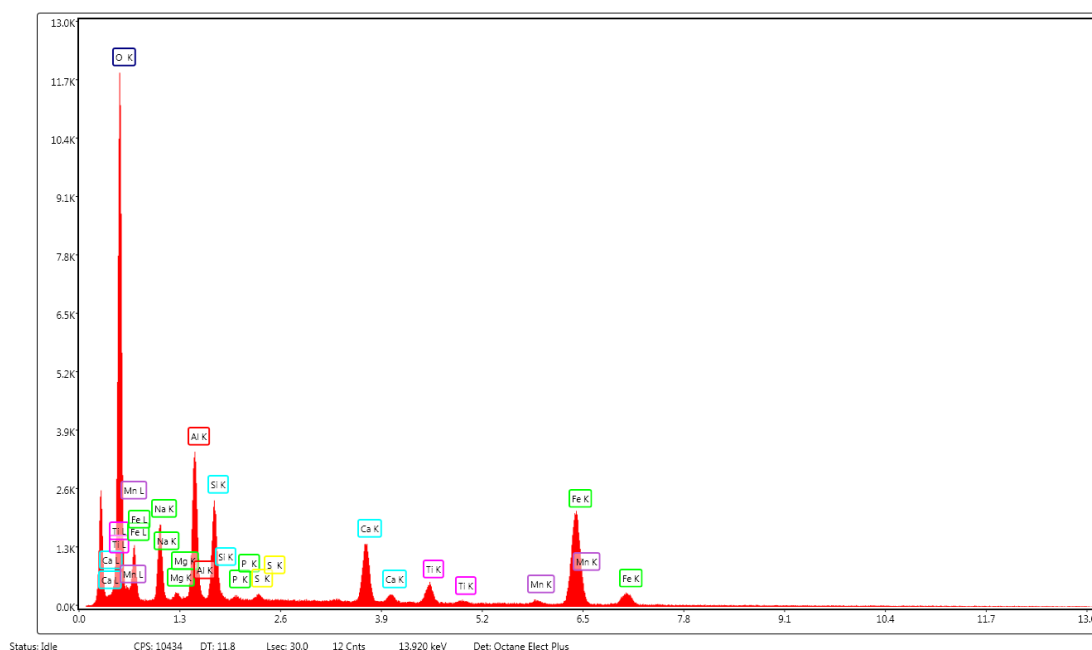
**Figure 3.3**  
Weight loss and “dm/dt” result of plastic waste containing paper



Regarding the samples with biomass and paper, the first decomposition peak was found in the range of 265-350 (with a maximum of 315°C) and 360-410°C (with a maximum of 390°C) using plastic containing biomass and around 240-343 (with a maximum of 310°C) and 389-436°C (with a maximum of 408°C) in case of plastic containing paper. Those peaks were caused by the cellulose decomposition (both cellulose and paper contain cellulose units). However, the decomposition took between 415 and 520°C was caused by the plastic constituents of the raw materials. The maximum of that peak was at 489°C in case of biomass and waste plastic mixture and at 487°C in case of waste plastic containing paper.

### 3.1.2. Catalysts

The EDAX result of the red mud is shown in **Figure 3.4**. Results showed, that the red mud consists of Fe (21.1%), Na (9.9%), Si (5.4%), Al (9.6%), Ca (5.7%), Ti (2.2%), Mg (0.9%), P (0.1%), S (0.3%), Mn (0.7%).



**Figure 3.4**  
The EDAX result of red mud

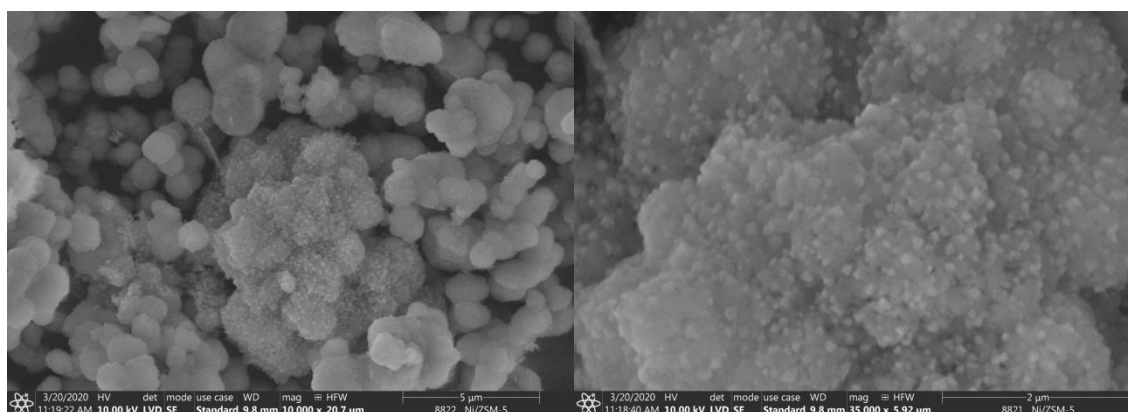
The  $\text{Ca(OH)}_2$  was supplied by the VWR International company. The structure of both the ZSM-5 (supplied from Alfa Aesar) and SAPO-11 (supplied from ZR Catalyst) catalysts was modified by nickel with the following proceeding. Catalysts were continuously stirred in 1 M  $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (provided by VWR International) at 80°C for 5 h, subsequently they were washed by deionized water, filtered and dried for 10 h at 110°C. In the

final stage, each catalyst was kept at 500 °C for 5 h. The main properties of the catalysts are summarized in **Table 3.2**. Ni/ZSM-5 had 15.1 Si/Al ratios, its BET surface was 324m<sup>2</sup>/g and has 1.55 nm average pore diameter.

**Table 3.2**  
The main properties of catalysts [276]

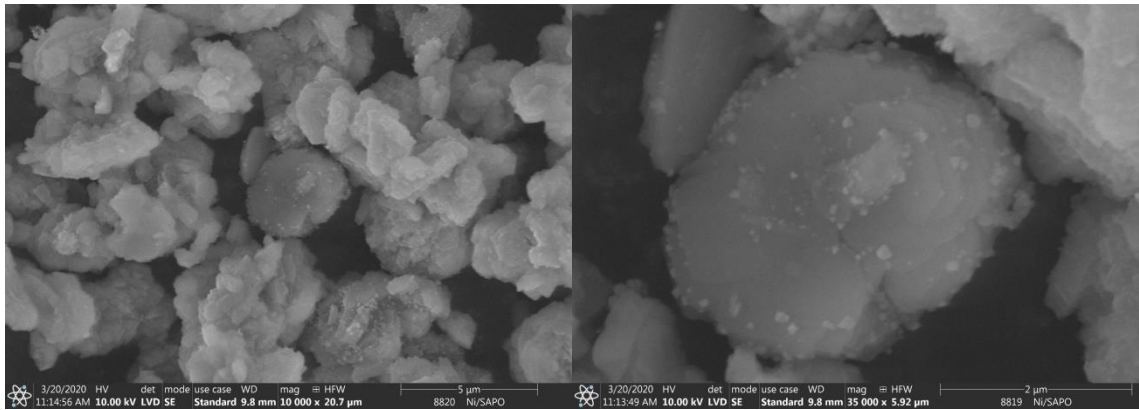
	Ni/ZSM-5	Ni/SAPO-11	Ca(OH) <sub>2</sub>	Red mud
<b>Appearance</b>	Light green powder	Light green powder	White powder	Red powder
<b>S<sub>BET</sub>, m<sup>2</sup>/g</b>	324	211	24.8	35.1
<b>S<sub>BJH</sub>, m<sup>2</sup>/g</b>	182	59	2.6	5.7
<b>Pore volume, cm<sup>3</sup>/g</b>	0.09	0.19	-	-
<b>Average grain size, μm</b>	1.5	2.2	5.7	5.1
<b>Si, %</b>	34.0	52.1	-	5.4%
<b>Al, %</b>	3.1	19.5	-	9.6%
<b>O, %</b>	55.2	1.0	43.2	44.6
<b>Ni, %</b>	6.5	6.1	-	-
<b>Other*, %</b>	Na (0.5%), Mg (0.4%), Ca (0.3%)	P (22.1%)	Ca (54%)	Fe (21.1%), Na (9.9%), Ca (5.7%), Ti (2.2%), Mg (0.9%), P (0.1%), S (0.3%), Mn (0.7%)

Ni/SAPO-11 catalyst had 0.25 Si/Al ratio, with 211m<sup>2</sup>/g BET surface and 2.11 nm average pore diameter. The catalyst had 6.1 (Ni/SAPO-11) and 6.5% (Ni/ZSM-5) nickel content, as the catalyst supporters were able to bind this amount of nickel during the impregnation of catalysts. The BET surface of the Ca(OH)<sub>2</sub> and red mud was 24.8 and 35.1 m<sup>2</sup>/g, respectively. The SEM micrographs of the catalysts are shown in **Figure 3.5**.

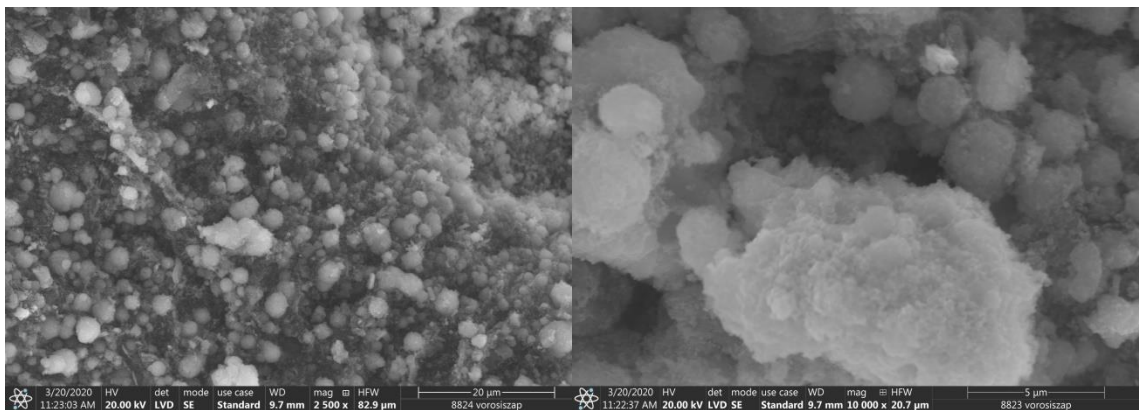


Ni/ZSM-5

**Figure 3.5**  
The SEM micrographs of the catalysts



Ni/SAPO-11



Red mud

**Figure 3.5**  
The SEM micrographs of the catalysts (cont.)

### 3.2. Comparison of different aging methods

The long term utilization of the hydrocarbon fractions is one of the main issues of the waste to fuel/energy processes. The longer-term properties of the hydrocarbon fractions, in general, are investigated via aging tests. It is also well known, that the parameters (e.g. temperature, atmosphere, treating time, etc.) had a noticeable effect on the result. In general, the pyrolysis oils are stored at 80°C till 1 day, however other methods are also available for following the aging properties. But, there is limited information and a critical evaluation of the connection regarding the different aging tests. The main aim of this part to make comparisons among the different aging tests to investigate the change in the properties of pyrolysis oil in long-term storage. A non-accelerated and accelerated aging test was implemented and then the viscosity, density, solid deposition and TAN have been compared.

The long-term properties of waste-derived pyrolysis oil were followed by both accelerated and non-accelerated aging tests. During the accelerated test, the pyrolysis oil was stored for 7 days at 80°C, while the same sample was kept at room temperature for 90 days in case of a non-accelerated test. The measurements were taken at 0, 1, 3, 5 and 7<sup>th</sup> days in case of accelerated aging test and at 0, 10, 30, 60 and 90<sup>th</sup> days in the case of a non-accelerated aging test.

The significance of the change in the results was followed by t-probe using the correlation coefficient, which was calculated using the following equation:

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x}) \cdot (y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2} \cdot \sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}} \quad (3.1)$$

Where “ $x_i$ ” and “ $y_i$ ” are the measured values, while “ $\bar{x}$ ” and “ $\bar{y}$ ” are their mean values. Besides, the significance of the correlation coefficient has been assessed by calculating the t-value.

$$t - value = \frac{r \sqrt{(n-2)}}{\sqrt{1-r^2}} \quad (3.2)$$

Where “ $r$ ” is the correlation coefficient, “ $n$ ” is the number of parallel measurements.

### 3.2.1. Pyrolysis oils

250 g of the raw materials were pyrolyzed in the one stage stainless steel batch reactor at 550°C (**Figure 2.3**). Under the used circumstances, pyrolysis oil was the main product (**Table 3.3**). Results show significant differences among the liquid hydrocarbon fractions. E.g. the TAN was below 0.05 mg KOH/g in case of HDPE, PP and PS raw materials, however, due to the oxygen-containing acidic components (aldehyde, ketones, carboxylic acid, etc.) it was considerably higher in case of MPW and MSW raw materials (1.1 mg KOH/g and 1.9 mg KOH/g). The density and viscosity were in the range of 0.835 g/cm<sup>3</sup> to 0.864 g/cm<sup>3</sup> and 2.17 mm<sup>2</sup>/s to 2.38 mm<sup>2</sup>/s, respectively, which was not significantly affected by the raw materials. Due to the linear structure of the polyethylene, pyrolysis oil from HDPE had the most n-paraffin (39.7%). Polypropylene has ramification in each second carbon atom in the main chain, therefore, the yield of branched-paraffin was the highest in the case of PP derived pyrolysis oil (27.4%). The same reason could be blamed

for the high aromatic content in the case of PS derived pyrolysis oil, because the polystyrene main chain has benzene rings as a side group. Hydrocarbons containing oxygen were found only in the case of MPW (8.3%) and MSW (18.2%) products.

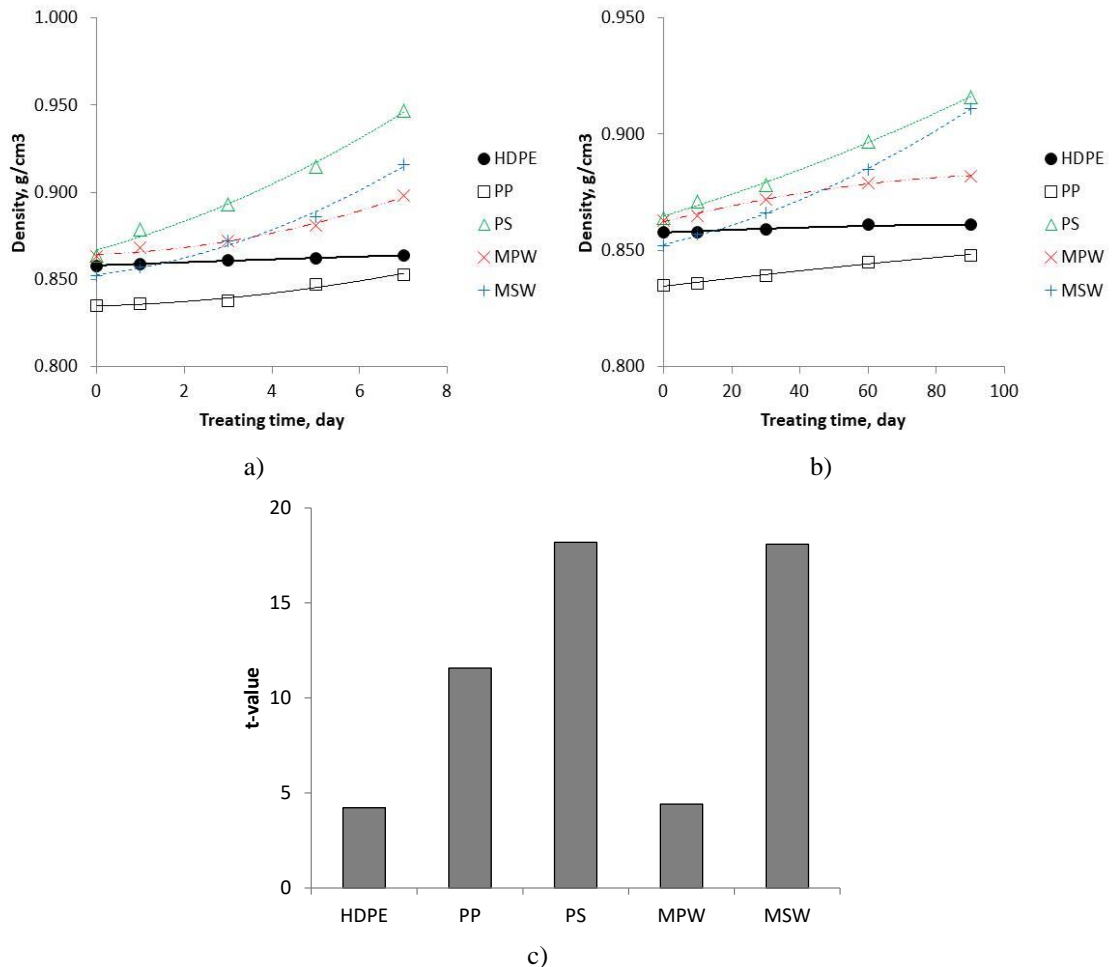
**Table 3.3**  
The main properties of pyrolysis oils

	HDPE	PP	PS	MPW	MSW
<b>Density, g/cm<sup>3</sup></b>	0.858	0.835	0.864	0.863	0.852
<b>Viscosity, mm<sup>2</sup>/s</b>	1.95	1.28	1.52	2.38	2.17
<b>TAN, mgKOH/g</b>	0.06	0.03	0.05	1.1	1.9
<b>Composition, %</b>					
<i>n-paraffin</i>	39.7	9.1	2.8	12.8	9.2
<i>Branched-paraffin</i>	8.9	27.4	5.1	19.5	14.5
<i>n-olefin</i>	42.5	12.5	4.7	17.3	7.3
<i>Branched-olefin</i>	6.3	49.2	3.5	22.4	19.4
<i>Monoaromatic</i>	n.d.	n.d.	72.8	12.5	9.2
<i>Polyaromatic</i>	n.d.	n.d.	8.3	2.7	11.5
<i>Oxygen containing</i>	n.d.	n.d.	n.d.	8.3	18.2
<i>Other/non identified</i>	2.6	1.8	2.8	4.5	10.7

### 3.2.2. Density

The density of the pyrolysis oils in the case of both accelerated and non-accelerated aging tests is summarized in **Figure 3.6**. Results well demonstrate that the densities were in the same range in the case of accelerated and non-accelerated tests (from 0.835 to 0.947 g/cm<sup>3</sup> and 0.835 to 0.916 g/cm<sup>3</sup>). The aging of PS and MSW derived pyrolysis oils resulted in the highest increasing rate in the density: 9.6% and 7.5% at the 7<sup>th</sup> day of the accelerated test and 6.0% and 6.9% at room temperature at the 90<sup>th</sup> day. Due to the presence of oxygen-containing compounds, a significant increase in the density was observed in the case of MPW and MSW derived pyrolysis oils aging. The best result was found when the HDPE sourced pyrolysis oil was treated, both by accelerated and non-accelerated ways. To compare the two different aging tests, lots of similarities were found, however, a linear correlation was found in waste plastics sourced oils in case of the non-accelerated tests, while the density change was close to exponential as regards to the pyrolysis oil achieved by MSW. On the other hand, the change of the density was exponential in the case of pyrolysis oils exclusively in the case of accelerated tests performed on HDPE sourced oils.

**Figure 3.6.c** demonstrates the result of significance analysis. According to results, each of the „t” value was over the  $t_{critical}$ , therefore the results of accelerated and non-accelerated aging are correlated. The best result (highest value) was found in case of PS derived pyrolysis oil (18.194), while the worst (lowest value) in case of MPW derived liquid fraction (4.223).



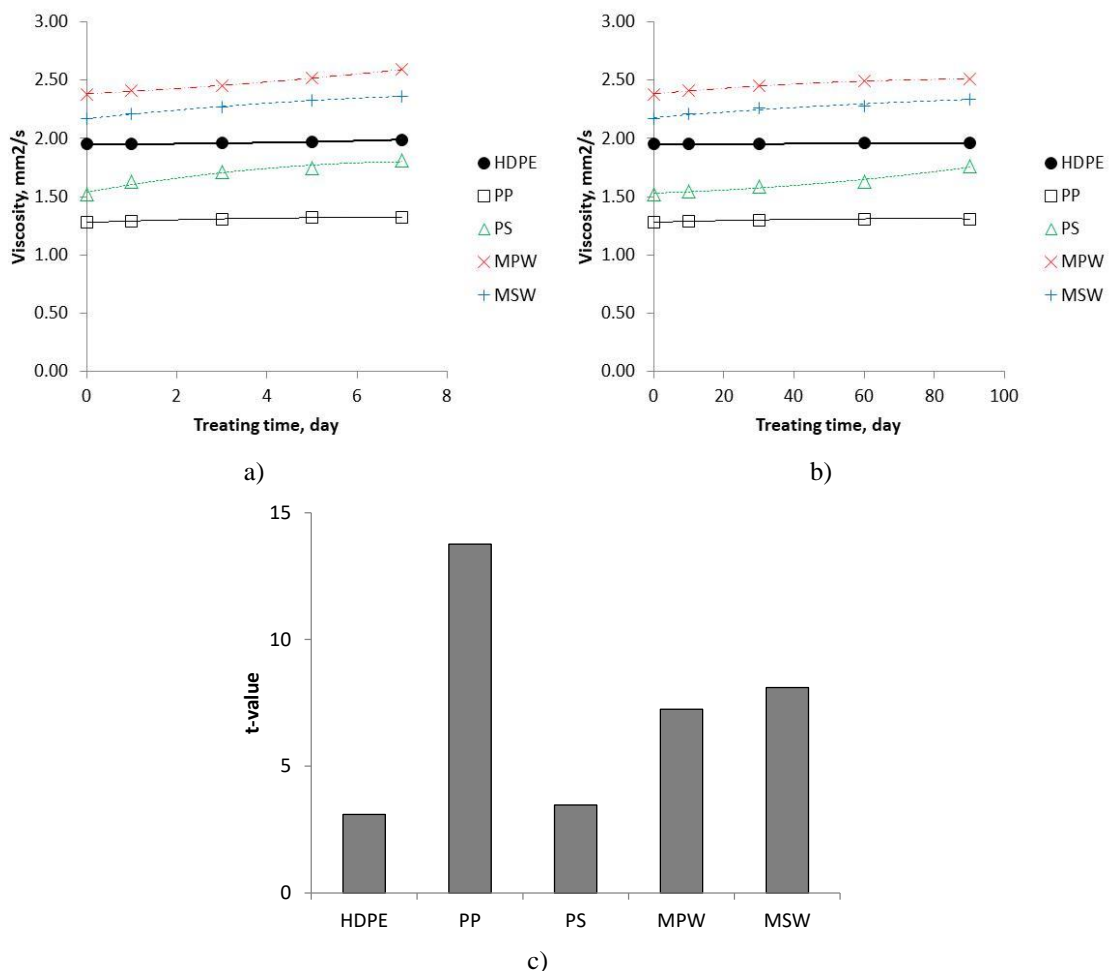
**Figure 3.6**

The density of pyrolysis oil during the accelerated aging (a) and the non-accelerated aging (b), significance analysis (c) ( $t_{critical}=2.571$  (95% confidence interval))

### 3.2.3. Viscosity

The viscosity of the pyrolysis oil is one of its most important properties because it directly influenced the pumping and transportation conditions. The viscosity of pyrolysis oils during the different aging tests is shown in **Figure 3.7**. In general, the pyrolysis of mixed raw materials resulted in a higher viscosity of pyrolysis oils (2.38-2.59 mm<sup>2</sup>/s (MPW) and 2.17-2.36 mm<sup>2</sup>/s (MSW)), than that of individual waste plastics (1.95-1.99 mm<sup>2</sup>/s (HDPE), 1.28 mm<sup>2</sup>/s-1.32 (PP), 1.52-1.81 mm<sup>2</sup>/s (PS)). It is also well shown, that

a moderate increase was found in the viscosity when the PS, MPW and MSW derived hydrocarbons were aged. This phenomenon was occurred by the reactive and unsaturated compounds, which can be interacted by different chemical reactions during the aging e.g. oligomerization, esterification, oxidization and polymerization, to produce larger molecules that led to increasing of the viscosity. Due to the limited availability of the unstable compounds, the viscosity of HDPE and PP sourced pyrolysis oils did not change considerably. As it was before mentioned, the well-shown correlation was found comparing the accelerated and non-accelerated aging. The significance analysis shows non-significant differences between the results obtained from accelerated and non-accelerated aging. The „t” value was in the range of 3.098 (HDPE)-13.760 (PP), which is higher than the critical value, which means that the differences between the accelerated and non-accelerated tests were not significant within 95% confidence interval.

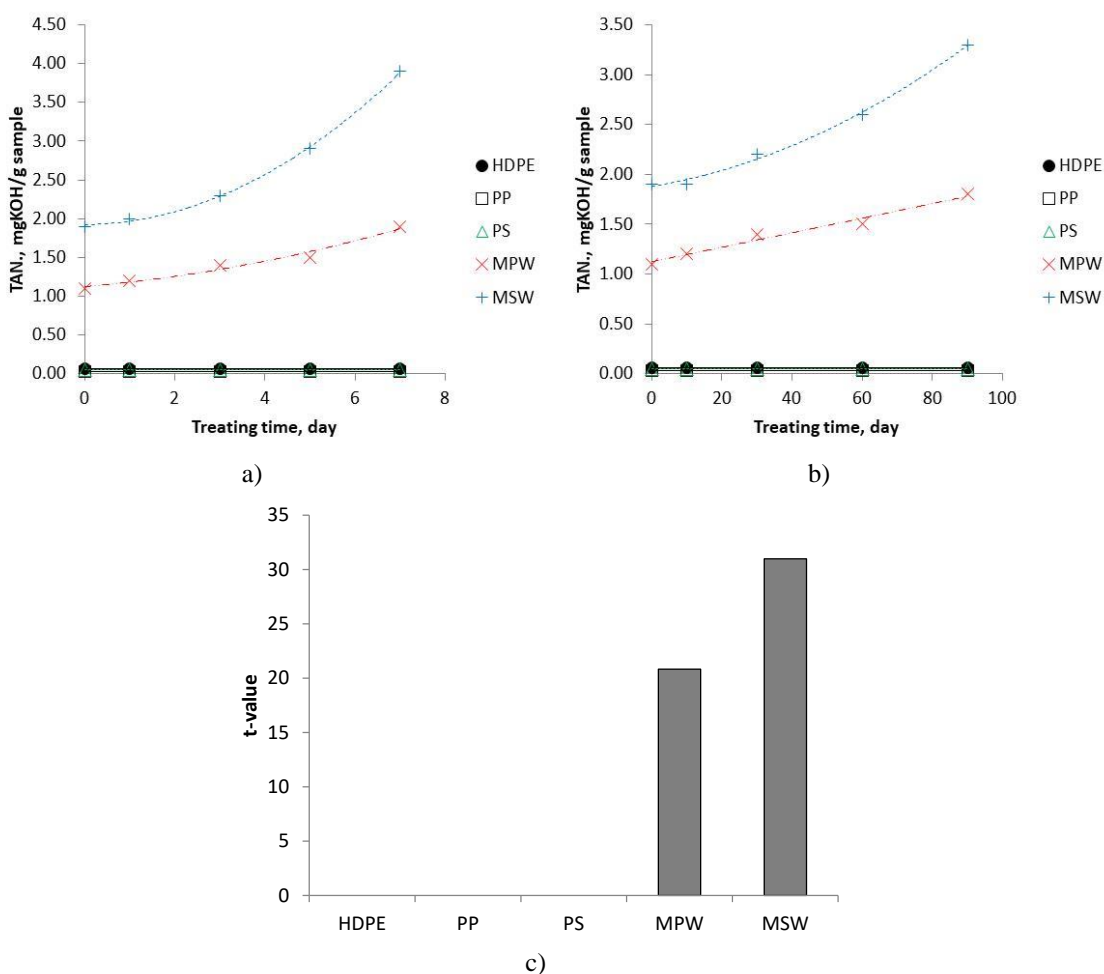


**Figure 3.7**

The viscosity of pyrolysis oil during the accelerated aging (a) and the non-accelerated aging (b), significance analysis (c) ( $t_{critical}=2.571$  (95% confidence interval))

### 3.2.4. Total Acid Number

The TAN of waste-derived pyrolysis oils are summarized in **Figure 3.8**. As **Table 3.3** well demonstrates, a plastic derived pyrolysis oil resulted in a fractions with the composition of n-paraffin, branched-paraffin, n-olefin, branched-olefin and aromatics hydrocarbons. Therefore the TAN was negligible in case of HDPE, PP and PS derived hydrocarbons. Furthermore, the acidity of these fractions did not change during aging.



**Figure 3.8**

The TAN of pyrolysis oil during the accelerated aging (a) and the non-accelerated aging (b), significance analysis (c) ( $t_{critical}=2.571$  (95% confidence interval))

The TAN of the MPW and MSW sourced light oils changed from 0.03-0.06mgKOH/g to 0.03-3.9 mgKOH/g (in case of accelerated aging) and to 0.03-3.3 mgKOH/g (in case of non-accelerated aging). On the other hand, biomass or oxygen-containing plastics (e.g. PET) in the raw material resulted in many of oxygenated compounds (acids, aldehydes, ketones, and phenols), which led to high acidity. The high acidity is unfavoured, due to its inconvenient corrosion properties. Not only the initial value



of the TAN was higher in the case of MPW (1.19 mg KOH/g) and MSW (1.1 mg KOH/g) derived pyrolysis oils, but also the change during the aging tests was also more significant. The change of the TAN belongs to MPW derived pyrolysis oils demonstrate linear function, while that of exponential in case of MSW sourced pyrolysis oils. For example, the TAN of the MPW and MSW sourced pyrolysis oils has increased by 72.7% and 105.3% in the 7<sup>th</sup> day of the accelerated aging or 73.7% and 63.6% at the 90<sup>th</sup> days in case of non-accelerated test.

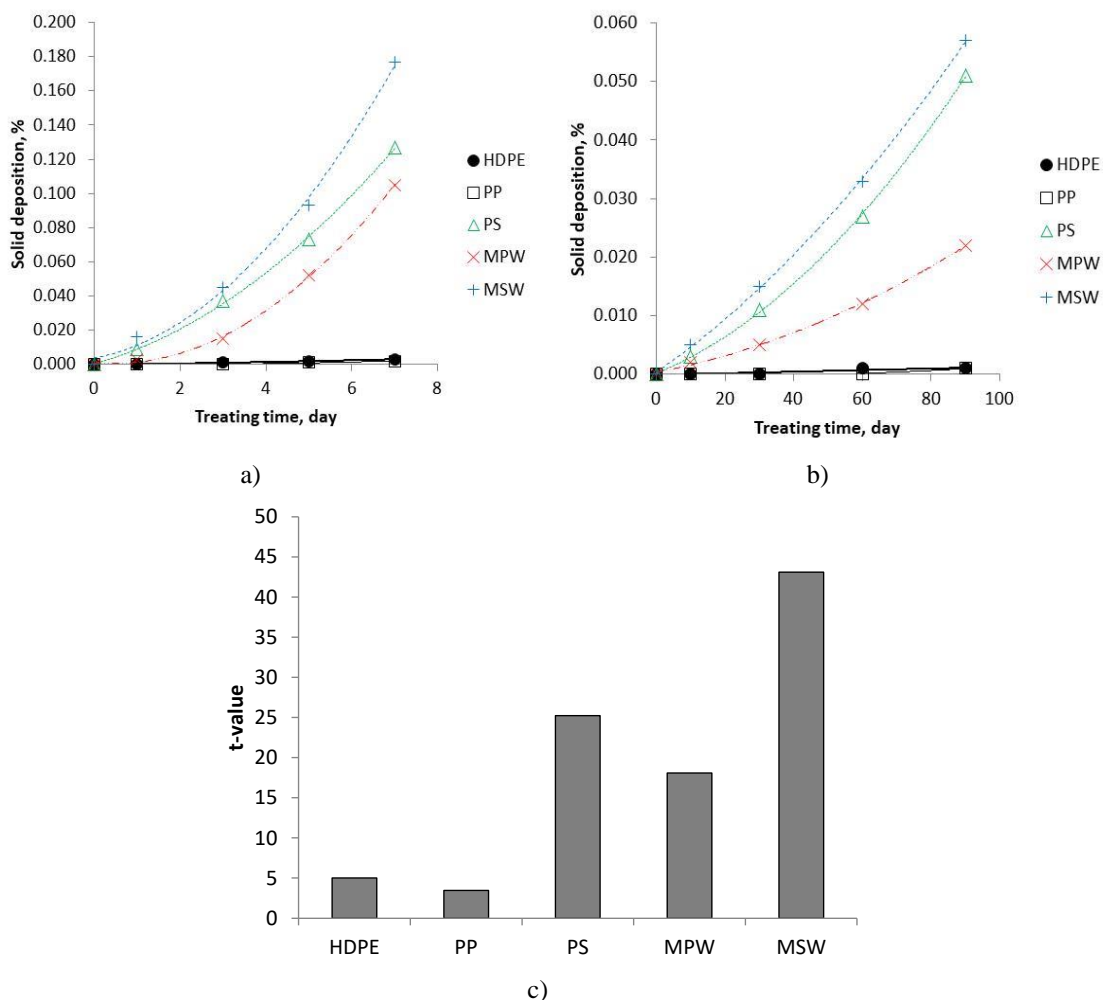
Comparing the two tests, it is clear that a good correlation was found. HDPE, PP and PS derived pyrolysis oils had no change in the TAN. Furthermore, the t-value was 20.821 (MPW) and 30.986 (MSW) in the two other cases.

### 3.2.5. Solid deposition

It is well known, that the different compounds in pyrolysis oils can be reacted and polymerized to higher molecular weight agglomerates under the aging circumstances. The amount of the molecule agglomerates should be followed by the solid deposition. *Figure 3.9* summarizes the change of the solid depositions as a function of the aging time in case of accelerated and non-accelerated aging.

Similarly, as it was before mentioned, HDPE, and PP derived pyrolysis oils had favorable properties regarding the formation of larger molecule agglomerates because the amount of the residue on the filter was less than 0.003% (HDPE) and 0.002% (PP). It means, that the olefins in the HDPE and PP derived pyrolysis oils can not be agglomerated into larger particles. On the other hand PS, MPW and MSW derived pyrolysis oils resulted in a more solid deposition during the aging tests. The increasing tendency was significant in each case of raw materials and both aging tests. E.g., the solid deposition increased from zero to 0.127%, 0.105% and 0.177% on the 7<sup>th</sup> day of the accelerated aging test and to 0.051%, 0.022% and 0.057% on the 90<sup>th</sup> day of the non-accelerated aging test, in case of PS, MPW and MSW originated pyrolysis oils, respectively. The disadvantageous aging characteristics of PS derived pyrolysis oils were primarily caused by the presence of the aromatic. Both monoaromatic and polyaromatic substances can result in larger molecular agglomerates by condensation and polycondensation reactions during aging. Comparing the two aging procedures, a well notable difference was found, because a more rapid change was observed in the case of accelerated aging test. This

indicates that the solid deposition on the filter after the 90<sup>th</sup> day in case of a non-accelerated test was equivalent to the result on the 3<sup>rd</sup> day of the accelerated test. That result is opposed with e.g. density and viscosity values because equivalence in both properties was concluded 90 days treating under non-accelerated conditions with 7 day treating at 80°C.



**Figure 3.9**

The solid deposition of pyrolysis oil during the accelerated aging (a) and the non-accelerated aging (b), significance analysis (c) ( $t_{critical}=2.571$  (95% confidence interval))

The calculated t-value was 5.000, 3.464, 25.231, 18.076 and 43.092 in the case of HDPE, PP, PS, MPW and MSW derived pyrolysis oils. It means that MSW derived pyrolysis oil results in the best correlation between the accelerated and non-accelerated tests, while PP derived the worst. However, PS and MPW derived pyrolysis oils showed also advanced correlation.

### 3.2.6. Main conclusions of the comparative study

The aging properties of the pyrolysis oils were significantly affected by the raw materials. The density and viscosity of the pyrolysis oils have increased to the highest degree in the case of PS and MSW raw materials. HDPE and PP derived pyrolysis oil showed better density and viscosity stability. Due to the aromatic hydrocarbons, pyrolysis oil from the PS decomposition had a significant increase in the viscosity and solid deposition. The oxygen-containing compounds significantly deteriorated the corrosion stability of the pyrolysis oils, because the TAN was greatly increased in both aging tests. Comparing the results of the accelerated and non-accelerated aging tests, it can be concluded that the density, viscosity and TAN on the 7<sup>th</sup> day during the accelerated aging test correlated well with the results on the 90<sup>th</sup> day of the non-accelerated test. However, in the case of solid deposition obtained at 80 °C after the 3<sup>rd</sup> day of the test, has correlated well with those obtained at room temperature on the 90<sup>th</sup> day. On the other hand, the correlation between the two tests was also affected significantly by the pyrolysis oil composition.

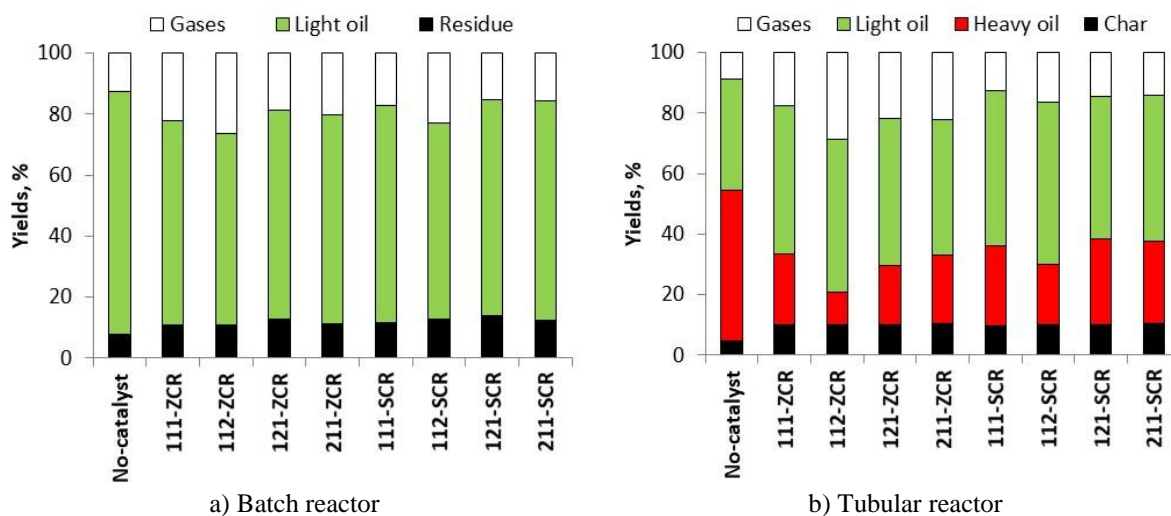
### 3.3. Pyrolysis of contaminated plastic waste

In this chapter chlorinated waste plastic was pyrolyzed in batch and tubular reactors using catalysts. The effect of the reaction parameters (e.g. reactors, catalysts) and the longer-term utilization of light oils was investigated and results concluded.

#### 3.3.1. Product yields

Owing to its direct influence on the feasibility and profitability of the waste to fuel processes, the product yield is a key parameter regarding the pyrolysis. The product yields of the pyrolysis of chlorinated real municipal plastic waste are summarized in *Figure 3.10*. It is clear, that the yield of volatiles was significantly increased by the use of catalysts. However, slightly less amount of light oil and higher yield of gaseous products were observed by the use of Ni/ZSM-5 based catalysts, like that of with Ni/SAPO-11 based catalysts, which was independent of the reactors (batch vs. tubular reactor). Due to the larger microporous surface area of ZSM-5 catalyst, the polymer decomposition was more significant causing in mainly more gaseous products. Furthermore, ZSM-5 zeolite has strong acidity and average pores (~5.5Å). However, SAPO-11 zeolite has weaker acidity and smaller pores (~3.8Å). It is also well shown, that ZSM-5 catalyst has a significantly higher Si/Al ratio. In general, a higher Si/Al ratio of acidic zeolite catalysts can lead to

more significant decomposition of C-C bonds, which increases the yield of light hydrocarbon and gases [276,277].



**Figure 3.10**  
The yields of pyrolysis products

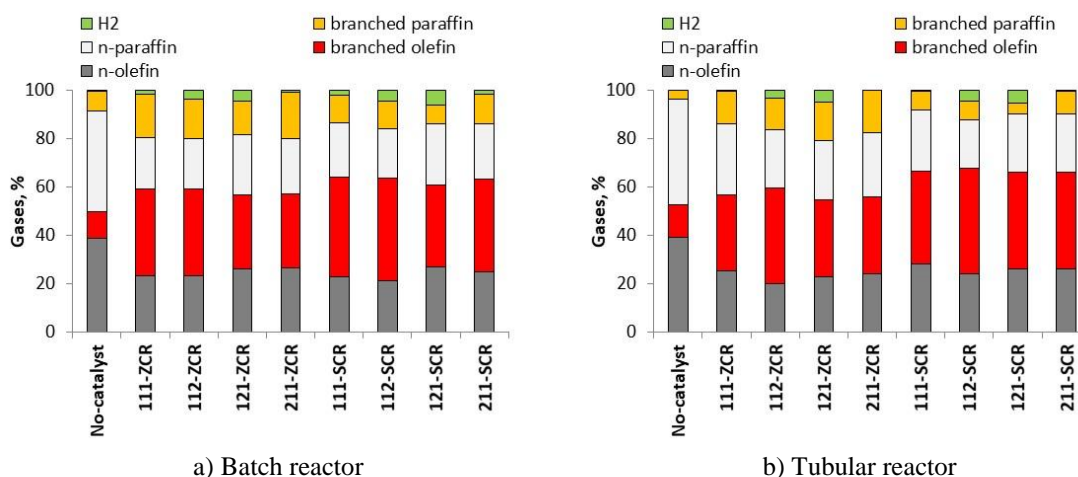
To compare the effect of the catalyst on volatiles yield, it appears that, both 112-ZCR and 112-S catalyst mixtures has the best performance in term of gaseous product and light oil production, which can be attributed to their high synthetic zeolite proportion. Red mud and  $\text{Ca}(\text{OH})_2$  mixed with synthetic zeolite have less influence on product yield structure. Therefore, the number of active centers of catalyst mixtures containing synthetic zeolite was reduced by introducing red mud and  $\text{Ca}(\text{OH})_2$ . Moreover, 211-ZCR and 121-SCR catalysts can increase the light oil yield. However, 111-ZCR and 111-SCR catalysts exhibited less efficiency in the production of gases. On the other hand, due to the remaining catalysts, the yield of char was higher in case of thermo-catalytic pyrolysis.

### 3.3.2. Products properties

#### 3.3.2.1. Gases

**Figure 3.11** summarizes the main composition of gases. Data well shown that the gas fraction contains especially hydrocarbons up to  $\text{C}_5$ . The n-paraffin and n-olefin hydrocarbons were the main components in gases, which can be attributed to the high concentration of polyethylene in the raw material (35% LDPE and 32% HDPE). Those components had been formed by  $\beta$ -scission reaction. The yield of branched hydrocarbons, such iso-butene, trans-but-2-ene, cis-but-2-ene, iso-butane, isopentane, 2,2-dimethylbutane and

methyl pentane can be considerably increased, as the result of the ion initiated isomerization reactions. In case of both reactors, SAPO-11 showed less efficiency in isomerization reactions, than ZSM-5 zeolite. ZSM-5 has a larger pore size comparing to SAPO-11, and the external diffusion of branched hydrocarbon was limited by using SAPO-11 based catalyst mixture. It should be pointed out, that the concentration of trans-but-2-en was higher by using Ni/ZSM-5 supporter, while a higher concentration of iso-pentene can be accomplished over Ni/SAPO-11 catalyst mixtures. High Ni modified synthetic zeolite content (112-ZCR and 112-SCR) can typically increase the yields of branched hydrocarbons both in case of Ni/SAPO-11 and in case of Ni/ZSM-5 supporters using both batch and tubular reactors. By comparing the catalyst mixtures, the adding of both  $\text{Ca}(\text{OH})_2$  and red mud declined the catalyst activity in isomerization reactions, which was attributed to the “diluting” effect of the red mud and  $\text{Ca}(\text{OH})_2$  which led to reasonably less number of catalyst active sites in the mass unit of the catalyst mixtures [276,277].



**Figure 3.11**  
The composition of gases

The hydrogen concentration was over 0.5% by only using 112-SCR, 112-ZCR and 121-SCR, 121-ZCR catalysts mixtures, which can be blamed by the synergetic effect of Ni loaded synthetic zeolite supported catalysts with red mud to the hydrogen yields. This effect was independent of the used reactor configurations, but the hydrogen content was a bit less in case of a tubular reactor. The synergetic effect was the consequence of the iron atom in the red mud, which can act as a promoter in a heterogenic catalytic reaction. This hypothesis was also described by Yao et al., who investigated the high-temperature pyrolysis of plastic wastes (HDPE, LDPE, PP, PS) using  $\gamma\text{-Al}_2\text{O}_3$  catalysts [278]. It has

been found that iron beside nickel could effectively increase the hydrogen yield. However, due to the lower temperature, the hydrogen concentration on gases was significantly lower in my case.

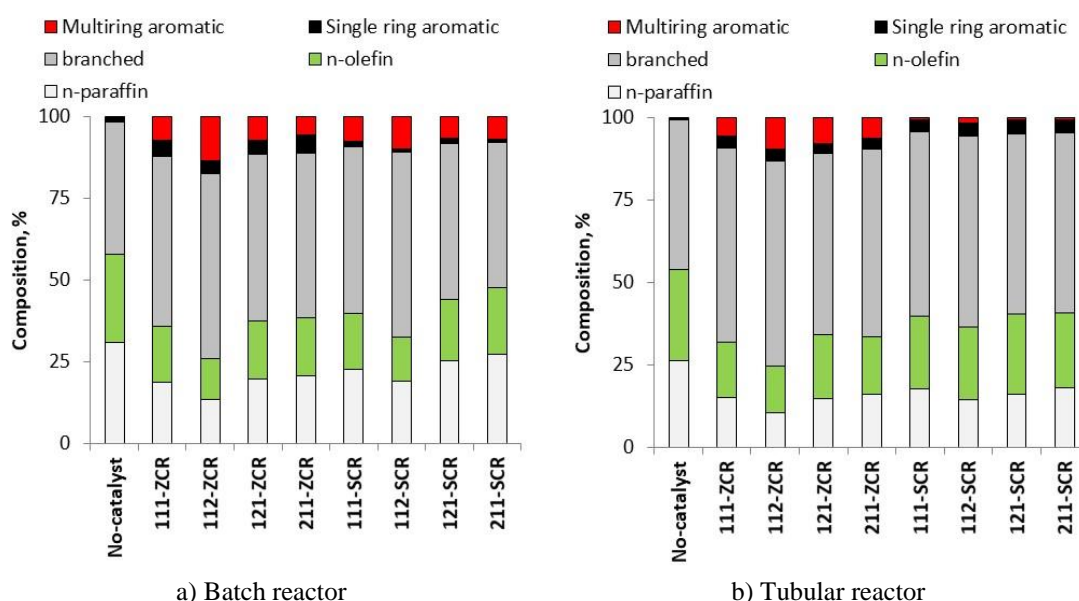
The amount of unsaturated compounds is increased while the concentration of saturated hydrocarbons is decreased by the use of catalysts. Conversely, the opposite tendency was found regarding the branched and non-branched hydrocarbons. The increase in the amount of unsaturated compounds was attributed to the greater extent of  $\beta$ -scission reactions on catalyst active centres. Due to this, the diffusion of molecules with greater hydrodynamic volume is limited in smaller pore size silicoaluminumphosphate molecule sieve; therefore the SAPO-11 catalysts have higher and better selectivity in the synthesis of unsaturated hydrocarbons. However, the small pore size inhibits the further isomerization of the unstable molecular fragments, therefore they are stabilized mostly in the unsaturated form [276,277].

Concerning the chlorinated compounds, chloroethane and chloromethane were identified in gases obtained from both batch and tubular reactors. The formation of chlorinated hydrocarbons in the pyrolysis products were established in earlier studies. E.g., a wide range of chlorinated hydrocarbons was identified when PVC has pyrolyzed alone [279]. Chloromethane was found in the pyrolysis products of wood and PVC mixture [280]. The summarized concentration of chlorinated organic components can decrease by the use of catalysts. Especially the high red mud and  $\text{Ca}(\text{OH})_2$  containing catalysts had a positive effect regarding the reduction of the chlorinated organic compounds. That phenomenon can be attributed to the alkali characteristic and the iron content and of the mentioned catalyst mixtures. It was previously established, that iron could promote the C-Cl scission and formation of halogenated transition metal oxides and other derivate or even HCl [281-287]. It is an important observation, that the SAPO-11 zeolite showed higher activity in term of de-chlorination comparing to ZSM-5. Owing to the higher Si/Al ratio, the ZSM-5 catalyst had higher activity both in C-C and C-Cl cracking, however, less amount of chlorinated compounds can be absorbed by ZSM-5 [276,277].

### 3.3.2.2. *Light oil*

Light oils had  $\text{C}_5\text{-C}_{35}$  hydrocarbons, but the cumulative concentration of  $>\text{C}_{24}$  compound was less than 2%. The composition of pyrolysis oils is summarized in **Figure 3.12**. As results well demonstrate, n-paraffin, n-olefin, branched, and aromatic (single ring and

multiring) compounds were contained in pyrolysis oils. The main fraction was the aliphatic compounds because the concentration of aromatic compounds was less than 17.6%. In one hand, the aromatization reactions can be enhanced by catalysts especially in case of the batch reactor. The concentration of aromatics was higher using a batch reactor, comparing to the tubular reactor, which can be attributed to the lower catalyst activity and shorter residence time in case of tubular pyrolysis. Owing to the longer residence time, the secondary reactions of aliphatic hydrocarbons resulting in their cyclization, aromatization and polymerization were more likely to occur in the batch pyrolysis.



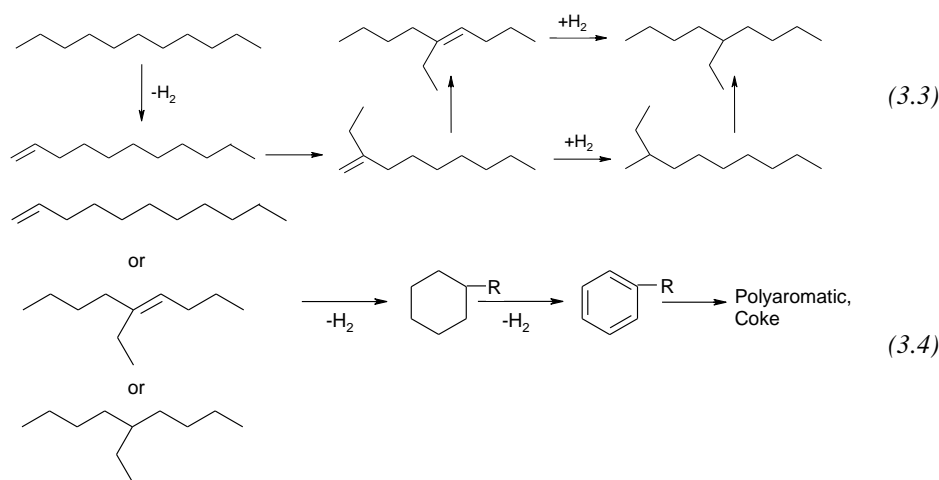
**Figure 3.12**  
The properties of light oils

It is worth mentioning that owing to the difference in catalyst pore size, the concentration of multi-rings aromatics was dominant in pyrolysis oils using Ni/ZSM-5 based catalysts, however, the concentration of single-ring aromatic was the dominant by using nickel loaded silicoaluminophosphate catalysts using tubular reactor. In case of batch reactor, the concentration of multiring aromatics was significantly higher than that of single ring aromatics [276,277].

It is also well known, the main chlorinated degradation product of PVC pyrolysis is the chlorobenzene [186,283]. It is an interesting result, that only a slight amount of aromatic compounds were produced without catalysts (less than 3%). However, the yield of aromatics could be significantly increased by catalysts. Lower aromatic concentration

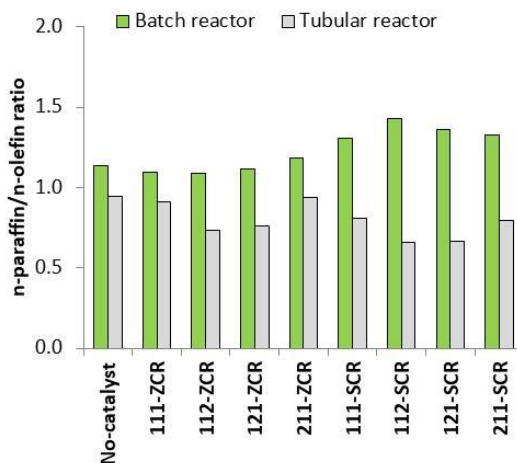
was obtained by silicoaluminophosphate catalysts and it was the result of the limited diffusion owing to the smaller pore size [276,277].

Both Ni/SAPO-11 and Ni/ZSM-5 based catalyst exhibited an advanced performance for carbon frame isomerization. The branched/(n-olefin+n-paraffin) ratio was 0.84 in case of thermal pyrolysis, while, the ratio increased to 1.35-1.59 (Ni/SAPO-11 based catalysts) and 1.62-2.51 (Ni/ZSM-5 based catalysts) in case of catalytic pyrolysis in a tubular reactor. More aromatic and less branched hydrocarbons were found in pyrolysis oils using a batch reactor system [276,277]. The possible reaction scheme of the catalytic isomerization and aromatization reactions are summarized in (3.3) and (3.4).



The n-paraffin/n-olefin ratio was slightly changed by using Ni/ZSM-5 catalyst mixtures in a batch reactor, however, a significant reduction was found in the case of Ni/SAPO-11 catalysts in case of the tubular reactor and increase by the using of the batch reactor (**Figure 3.13**). The n-paraffin/n-olefin ratios were 1.14 (batch reactor) and 0.94 (tubular reactor). That value has changed to 1.09-1.18 (batch reactor, Ni/ZSM-5 based catalysts), 0.73-0.93 (tubular reactor, Ni/ZSM-5 based catalysts), 1.30-1.43 (batch reactor, Ni/SAPO-11 based catalysts) and 0.66-0.82 (tubular reactor, Ni/SAPO-11 based catalysts). It means that the Ni/SAPO-11 based catalysts has resulted in lower n-paraffin/n-olefin ratios than Ni/ZSM-5 based. It is also important to remark, that the lowest values were found in the case of 112-ZCR and 112-SCR marked catalysts. However, the change in the ratio was also affected by the amount of branched hydrocarbons.





**Figure 3.13**  
The n-paraffin/n-olefin ratio of light oils

The main properties of the light oils are summarized in **Table 3.4**. The density and viscosity changed in the range of 0.759-0.847 g/cm<sup>3</sup> and 1.041-1.905mm<sup>2</sup>/s respectively. The flash point was below 50°C. Due to chlorine in raw materials, 228-5509ppm chlorine was found in light oils. The TAN values of the liquid fractions was between 2.1 and 11.5mgKOH/g sample. The density, viscosity, chlorine content and TAN can be decreased by catalysts.

**Table 3.4**  
Main properties of light oils obtained by pyrolysis of chlorinated waste plastics

		No-cat- alyst	111- ZCR	112- ZCR	121- ZCR	211- ZCR	111- SCR	112- SCR	121- SCR	211- SCR
<b>Batch reactor</b>	<b>Colour</b>	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish
	<b>Density, g/cm<sup>3</sup> (at 20°C)</b>	0.847	0.787	0.773	0.784	0.779	0.796	0.782	0.793	0.781
	<b>Viscosity, mm<sup>2</sup>/s (at 20°C)</b>	1.905	1.246	1.081	1.185	1.202	1.372	1.115	1.297	1.207
	<b>Flash point, °C</b>	<50	<50	<50	<50	<50	<50	<50	<50	<50
	<b>TAN, mgKOH/g</b>	7.9	3.5	4.3	2.9	2.7	3.3	4.2	2.1	2.5
	<b>Chlorine, ppm</b>	4364	2083	1344	485	284	1208	1284	377	228
<b>Tubular reactor</b>	<b>Colour</b>	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish
	<b>Density, g/cm<sup>3</sup> (at 20°C)</b>	0.811	0.775	0.759	0.772	0.763	0.785	0.771	0.773	0.781
	<b>Viscosity, mm<sup>2</sup>/s (at 20°C)</b>	1.781	1.172	1.041	1.075	1.124	1.217	1.074	1.126	1.159
	<b>Flash point, °C</b>	<50	<50	<50	<50	<50	<50	<50	<50	<50
	<b>TAN, mgKOH/g</b>	11.5	4.8	5.5	3.6	3.8	4.2	5.1	2.9	2.8
	<b>Chlorine, ppm</b>	5 509	2 619	1 804	645	342	1 897	1 724	528	327

### 3.3.2.3. Heavy oil

Heavy oil was obtained as the bottom product of the fractionation in case of pyrolysis using tubular reactor. It has brown in colour and solid, grease-like appearance. The main properties of the heavy oils are summarized in **Table 3.5**.

**Table 3.5**  
Main properties of heavy oils obtained by pyrolysis of chlorinated waste plastics

	No-catalyst	111-ZCR	112-ZCR	121-ZCR	211-ZCR	111-SCR	112-SCR	121-SCR	211-SCR
Density, g/cm <sup>3</sup> (at 100°C)	0.855	0.822	0.806	0.841	0.834	0.828	0.816	0.832	0.829
Viscosity, mm <sup>2</sup> /s (at 100°C)	6.88	5.64	5.01	5.95	5.62	5.42	5.15	5.28	5.38
Melting point, °C	91	84	83	85	84	84	83	87	86
Flash point, °C	221	215	201	210	214	212	209	210	216
IBP, °C	158	153	152	151	152	153	158	157	155
FBP, °C	>350	>350	>350	>350	>350	>350	>350	>350	>350
Caloric value, MJ/kg	41.6	41.9	41.8	41.7	41.3	41.9	41.8	41.8	41.5

The density and viscosity show a significant difference. Pyrolysis without catalysts has a high density (0.855 g/cm<sup>3</sup>). It is clear, that the density can be reduced by catalysts to the range of 0.806-0.841 g/cm<sup>3</sup> in case of Ni/ZSM-5 based catalysts mixture and to the range of 0.816-0.832 g/cm<sup>3</sup> using Ni/SAPO-11 based catalysts mixtures.

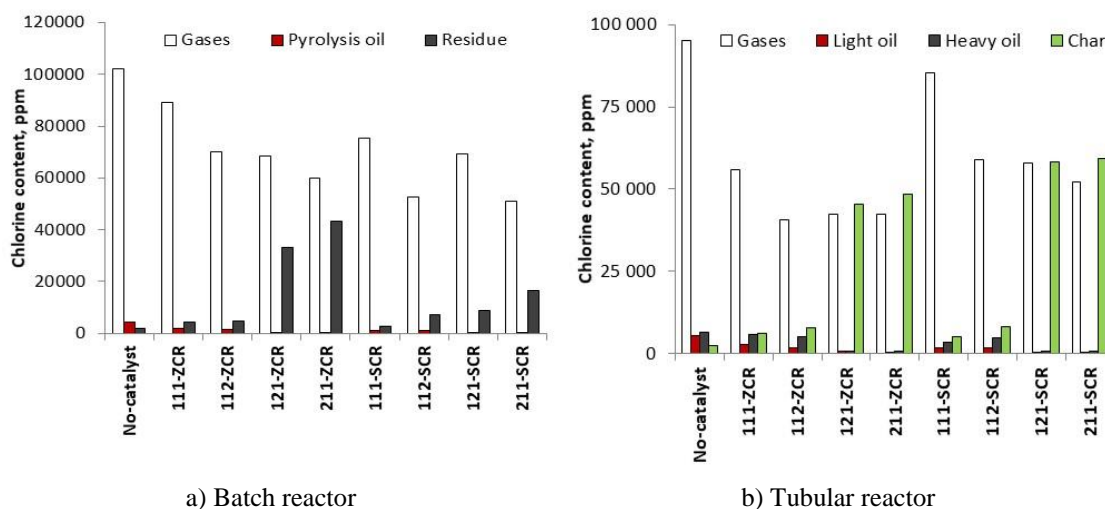
The viscosity was 6.88 mm<sup>2</sup>/s without catalyst at 100°C and the catalysts can result lower viscosity. Therefore, the using of catalysts has a positive effect on the heavy oil by reducing of it density and viscosity.

The melting point of heavy oil has a slight difference between the catalyst free and thermo-catalytic pyrolysis. The melting point was 91°C and 83-87°C absence and in the presence of catalysts, respectively. The value of flash point can be also decreased by catalysts, especially by Ni/ZSM-5 based catalysts mixture. However, regarding the HHV, no significant difference was concluded by the catalyst application, because the values were in the range of 40.3-41.9 MJ/Kg [277].

### 3.3.2.4. Chlorine content

In regards to the long-term application of pyrolysis products, the concentration of contaminants (e.g. chlorinated compounds) is considered as a crucial factor. In general, hydrocarbons with fewer contaminants have advantageous long-term properties. The

chlorine content of pyrolysis products is summarized in **Figure 3.14** [276,277]. As illustrated in the figure, light oils from catalyst-free pyrolysis have high chlorine content; however, the chlorine content of volatiles was significantly decreased by the use of Ni/ZSM-5 catalysts.

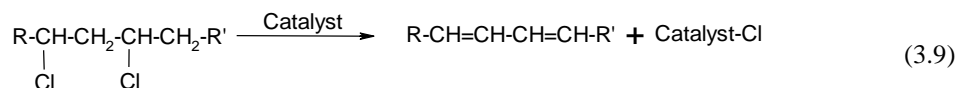
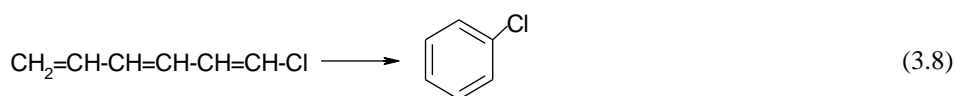
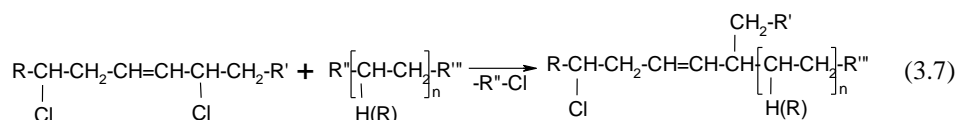
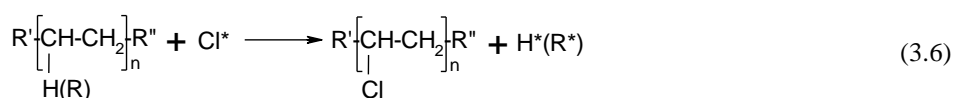
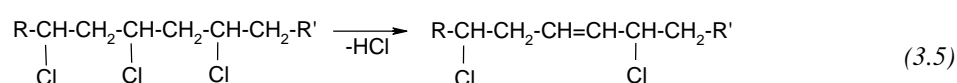


**Figure 3.14**  
The chlorine content of the products

Results well demonstrate that the silicoaluminophosphate supported catalyst mixtures have higher efficiency in chlorine reduction than ZSM-5 supported catalysts. However, the chlorine content of pyrolysis oil can be significantly reduced by catalysts, especially with high  $\text{Ca}(\text{OH})_2$  and red mud content. It is worth mentioning, that in both cases (batch and tubular reactor), the high red mud content is seen as the most convenient method for decreasing the chlorine-containing compounds. The helpful effect of iron compounds (e.g. red mud,  $\text{FeCl}_3$ , hematite) for chlorine removal was defined earlier and the advantageous property was accredited to the sorption of chlorinated hydrocarbons on the surface of the ferrous materials or the cracking of C-Cl bond [284-287,290-292]. In terms of the long-term fuel applicability, the catalysts with high alkaline content were the most effective, owing to its ability in reducing the chlorine content in the products, which results in more appropriate in terms of transportation and storage characteristics [276,277].

By comparison of the two different reactor systems, it is clear that the batch reactor produced gases with lower chlorine content, while a higher chlorine content liquid products were produced by the tubular reactor. This implies that the favorable long-term fuel purposes hydrocarbons could be produced in batch reactor rather than the tubular process using chlorinated polyolefins [276,277].

The PVC decomposition starts at a lower temperature than comparing to the C-C scission of both polyethylene and polypropylene. In the first reaction step, the C-Cl bond in PVC macromolecule begins to decompose around 300-350°C with chlorine or chlorinated radicals. Then those radicals can further take part in the decomposition of other plastics, such as polyethylene or polypropylene. One of the possible ways for the stabilization of molecule fragments from PVC or other plastics is the formation of chlorinated hydrocarbons or HCl (partial dechlorination by HCl formation (3.5), chlorination (3.6), dechlorination by recombination (3.7), chlorinated aromatic formation (3.8), dechlorination by catalysts (3.9)) [276,277].



Due to the operation specific of the continuous pyrolysis process, there is no possibility for “stepwise-like” pyrolysis in continuous pyrolysis using a tubular reactor. The mixture of the polymers is continuously fed into the reactor using a screw. The PVC in the raw materials started to decompose in the beginning section of the reactor almost during their heating up period, but the chlorine radicals cannot leave the tubular reactor till all of the raw material reaches the set temperature. Consequently, the chlorine remains inside the reactor and can play an active role in the further decomposition of other plastics resulting higher amount of chlorinated (organic) compounds. Contrary, the PVC can decompose in a large part during the reactor heating period, and chlorinated products (especially HCl) can leave the reactor vessel before the other polymer start to decompose. The role of the catalysts was primary to sorb the chlorine-containing compounds and reduce the activation energy of the C-C and C-Cl scission [276,277].

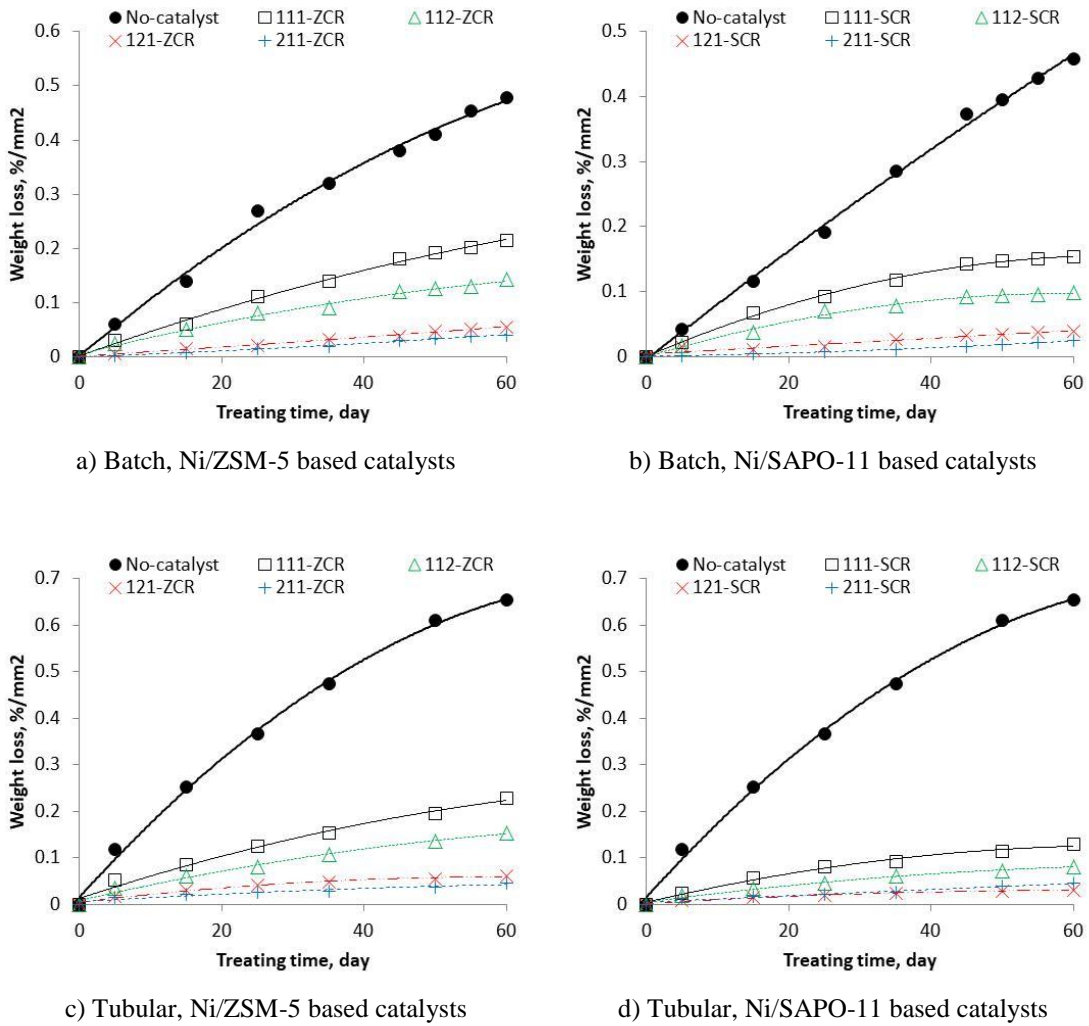
The bottom product of the distillation column also contained solid substances (in form of inorganic filler, catalyst or coke, etc.) which were separated by a hot press filter. Under all circumstances, light oil had less chlorine content by comparing it to the heavy oils, which were produced under the same conditions. Catalysts can absorb the chlorine-containing compounds; therefore, the chlorine content of solid residues obtained by thermo-catalytic pyrolysis can be increase radically. Due to the sorption of the chlorine-containing compounds on the catalysts surface the largest chlorine content of the solid residues were found when  $\text{Ca}(\text{OH})_2$  and red were used. In these cases, not the C-Cl cracking, but the sorption of the high specific surface catalyst mixtures was the determining factor. Meanwhile, it can be assumed that the chlorine content of the solid residues was higher in each case using the SAPO-11 catalysts, therefore those catalysts have high activity for dechlorination [276,277].

### **3.3.3. Longer-term properties**

#### **3.3.3.1. Corrosion test**

In order to investigate the corrosion properties of liquid products, a copper plate had been stored for 60 days in the liquid hydrocarbons and then the weight loss was measured (*Figure 3.15*).

The weight loss was less in case of batch reactor but only without catalysts. Therefore the light oil from batch reactor had better corrosion property, than that of from tubular reactor in case of catalyst-free pyrolysis. The concentration of chlorinated organic compounds is responsible for this phenomenon. Unexpectedly, the pyrolysis oils obtained by thermo-catalytic pyrolysis in tubular reactor resulted in relatively less weight loss, comparing to that using batch reactor. E.g. the weight loss at the 60<sup>th</sup> day occurred by thermo-catalytic pyrolysis derived light oil was 4.7-19.6% (Ni/SAPO-11 based catalyst mixtures) and 6.7-30.8% (Ni/ZSM-5 based catalyst mixtures) of the weight loss in case of the non-catalytic pyrolysis using tubular reactor. Regarding the light oil from batch reactor, those values were 5.4-33.4% (Ni/SAPO-11 based catalyst mixtures) and 8.1-44.5% (Ni/ZSM-5 based catalyst mixtures).

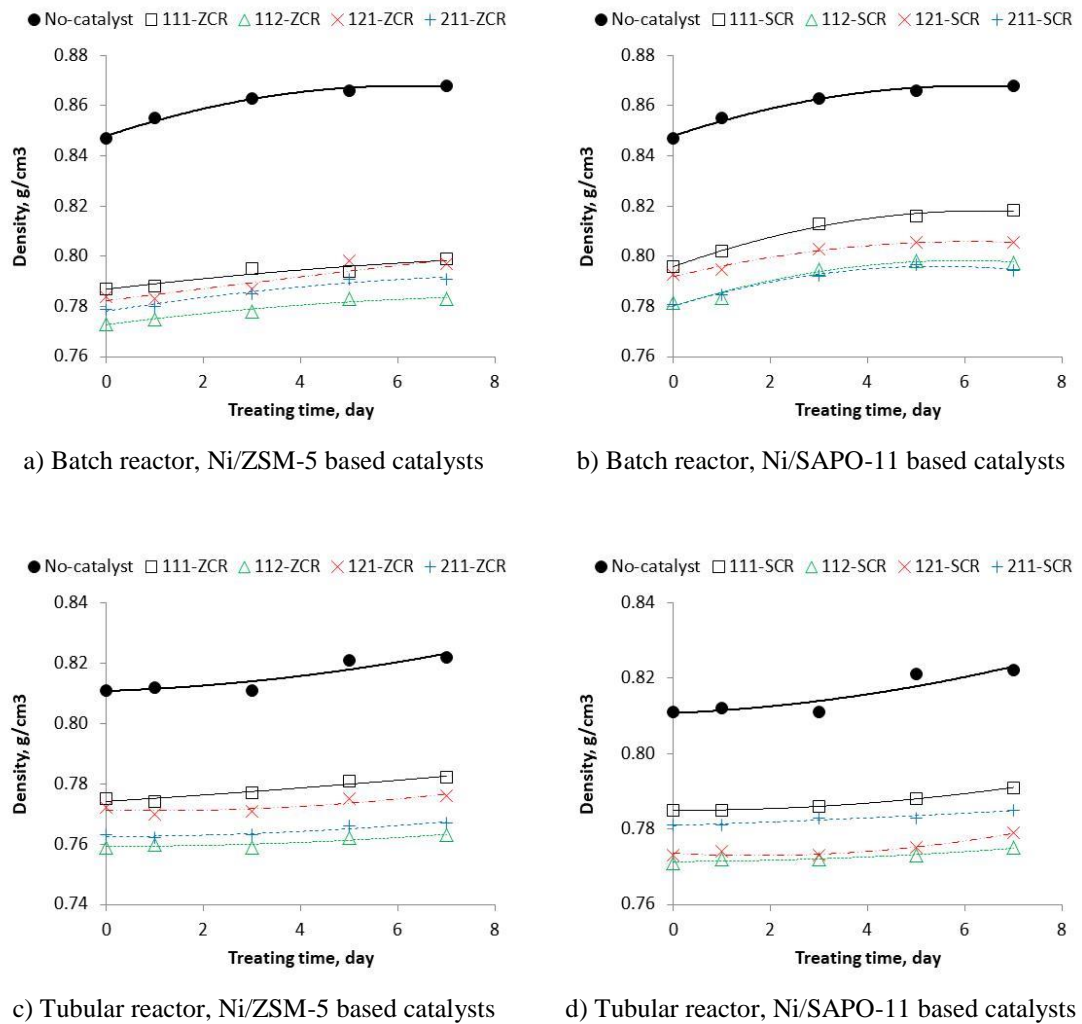


**Figure 3.15**  
Weight loss of the copper plate sample during the corrosion test

It is also an important observation, the weight loss in the case of a tubular reactor can be considerably reduced by the 121-Z and 121-S catalysts. Presumably, the high iron concentration in red mud favorably modified the product structure by reducing its chlorine content, which can prevent further substantial corrosion problems in case of the long-term handling. The corrosion test has proved that the high alkali content of the catalysts is preferred for long-term storage and transportation of fuels from PVC containing waste plastic since the weight loss of the copper plates is considerably reduced [276,277].

### 3.3.3.2. Accelerated aging test

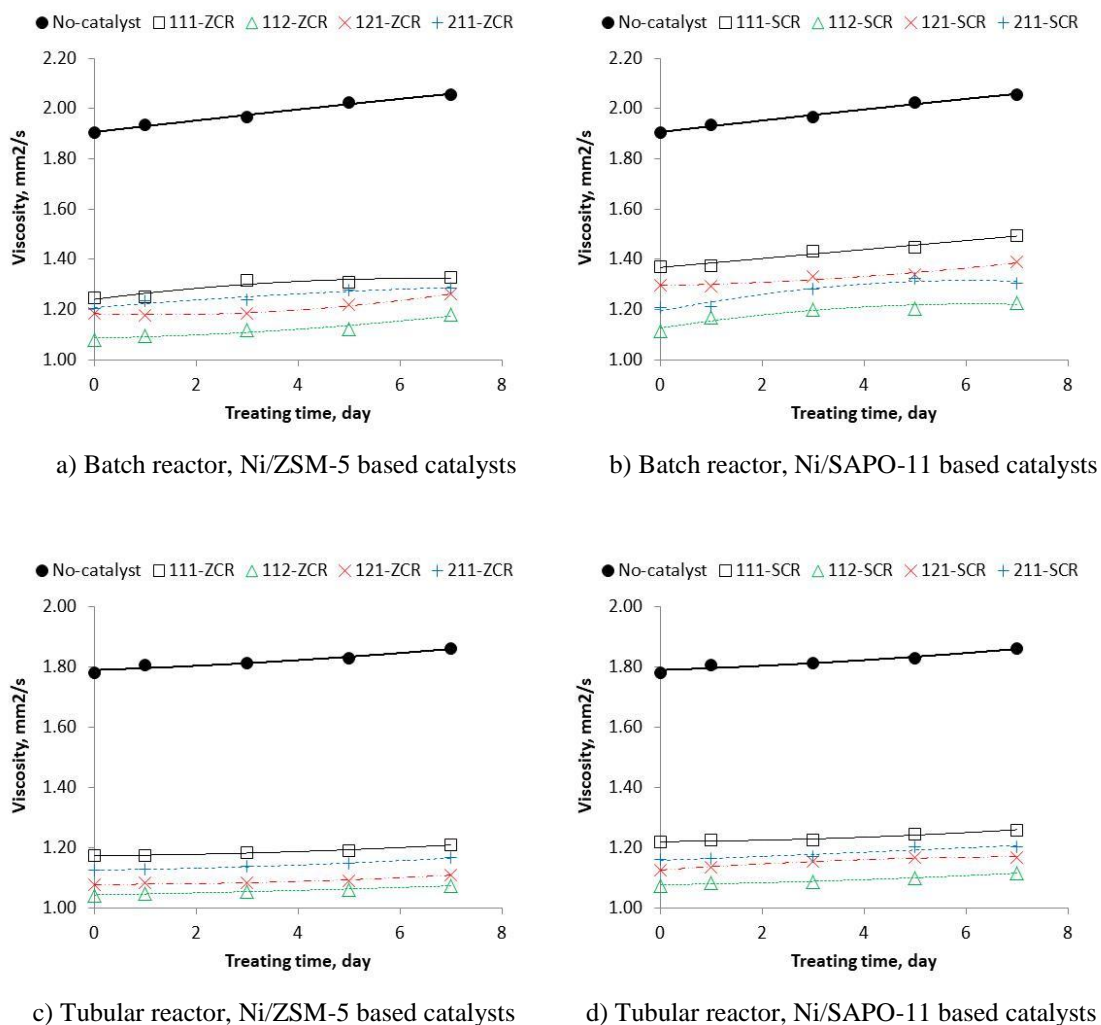
Accelerated aging test was performed to investigate the long-term application of light oil. According to results, the density and the viscosity slightly increased as function of aging (*Figures 3.16 and 3.17*).



**Figure 3.16**  
The density of pyrolysis oils during the aging test

It is clear, that a higher increasing rate was found in the case of the thermal pyrolysis process using both batch and tubular reactors rather than in the thermo-catalytic process. However, it can be concluded that the catalysts had a beneficial effect on both properties because light oil from catalytic pyrolysis processes had fewer changes in viscosity and density. E.g. the density increased by 2.59% without catalysts and 1.28-1.78% with Ni/SAPO-11 and by 1.31-1.65% with Ni/ZSM-5 catalysts during the 7<sup>th</sup> days treating using tubular reactor. Regarding the batch reactor, the density of pyrolysis oil without

catalysts increased by 1.99% at the 7<sup>th</sup> day of the treating at 80°C. On the other hand, it can be increased by 2.03-2.68% using Ni/ZSM-5 catalysts, or 2.57-3.06% using Ni/SAPO-11 catalysts [276,277].

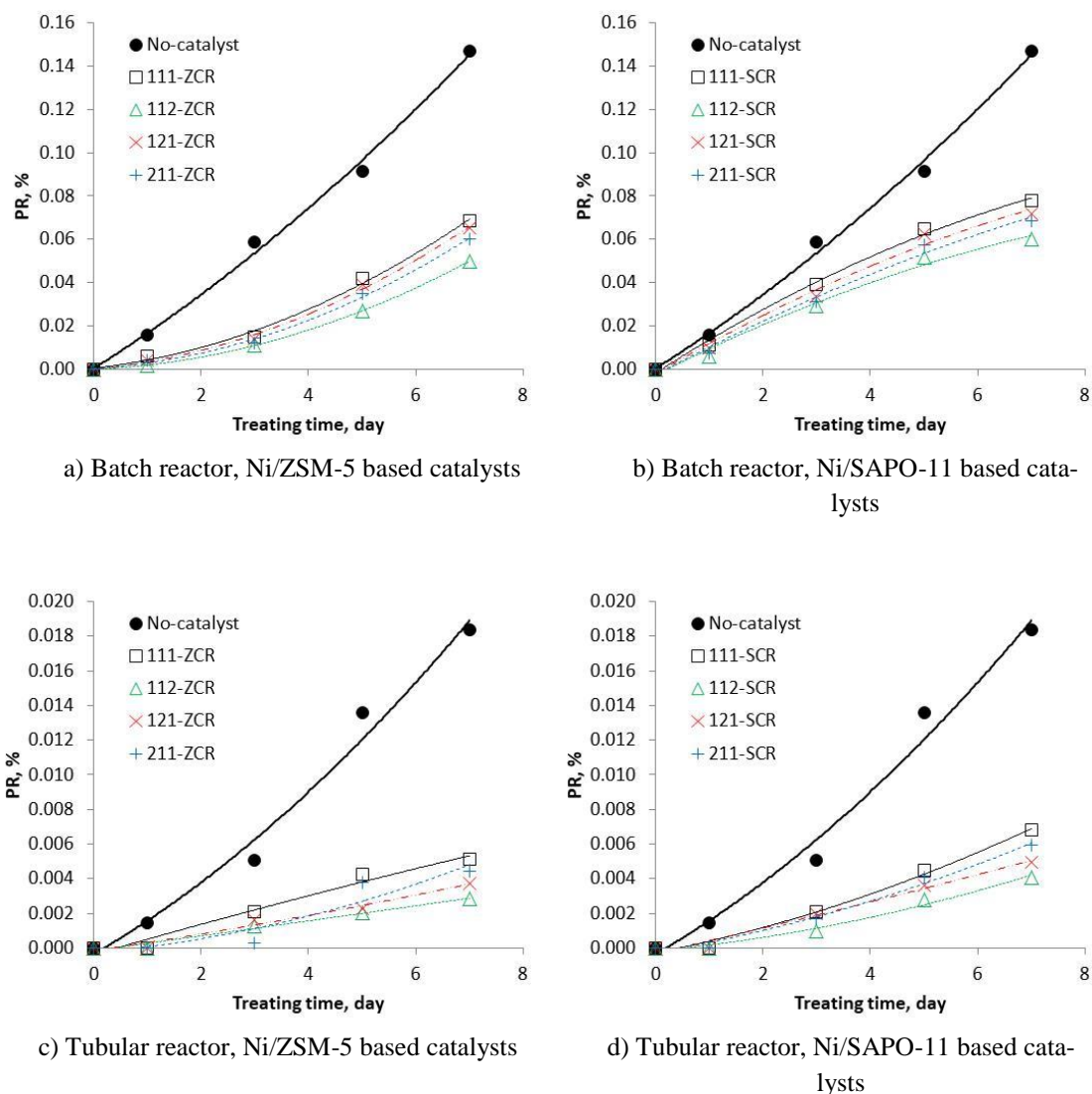


**Figure 3.17**  
The viscosity of pyrolysis oils during the aging test

Similar phenomena were concluded regarding the viscosity, however, the increasing ratio was higher. This indicates that the molecule forming agglomerates resulting in higher density and viscosity was not substantial during the aging, which is worthwhile for the long-term fuel-like utilization of light oils. It is important to remark, that the same order of catalysts efficiency was found regarding the density and viscosity increasing in case of both Ni/ZSM-5 and Ni/SAPO-11 catalysts: 121, 211, 111 and 211 [276,277].

The amount of oligomer-polymer phase separated from the light oil during the accelerated aging test is summarized in **Figure 3.18**.





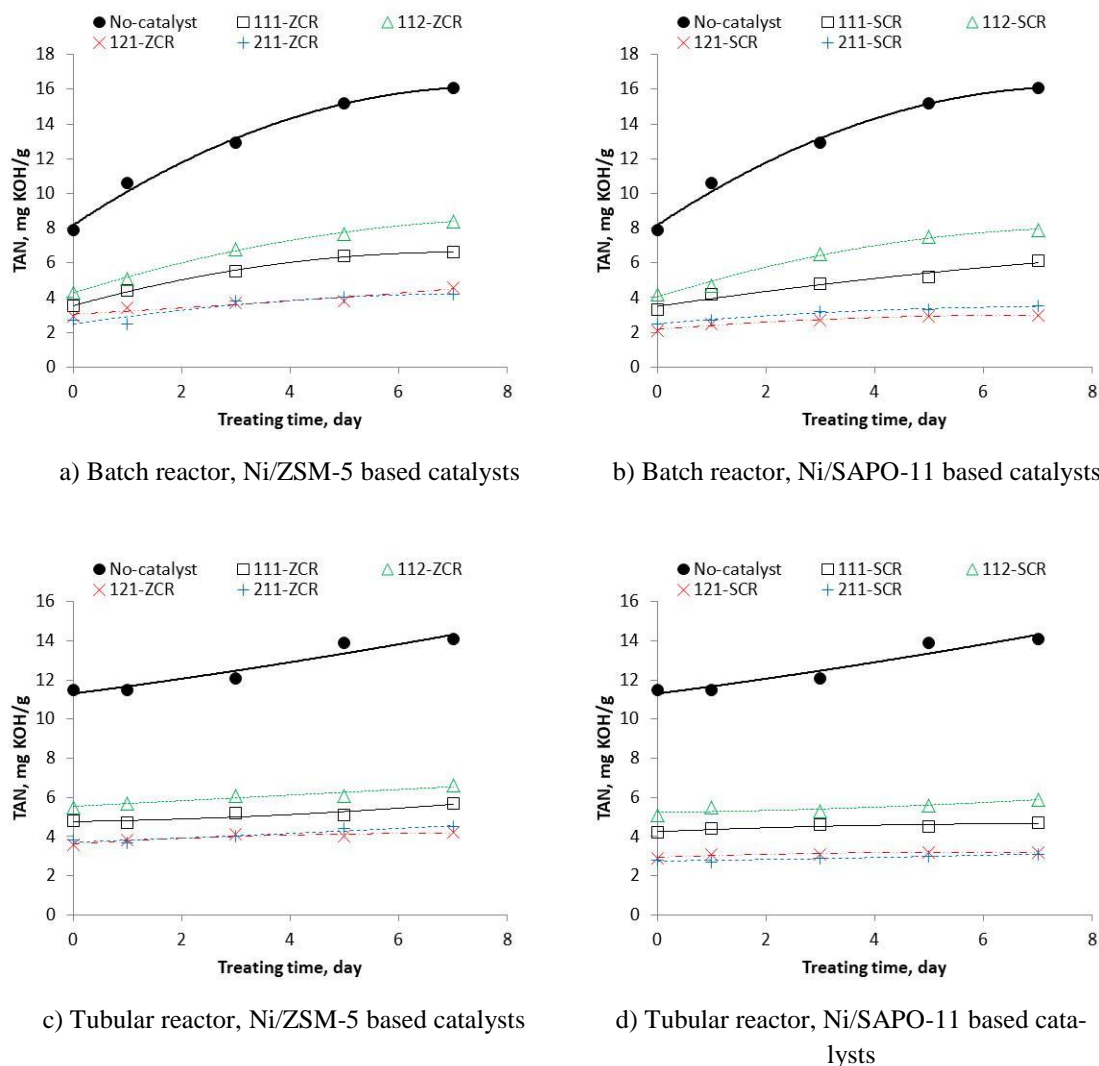
**Figure 3.18**  
Polymer-oligomer residue on the filter after the aging test

In both thermal and thermo-catalytic pyrolysis, an increasing tendency was found independently from the used reactor. At the end of the 7<sup>th</sup> day, the amount of substances remaining on the filter was 0.15% (batch reactor) and 0.018% (tubular reactor) without catalysts. It means, that significantly lower change was concluded by the use of catalysts. E.g. it was 0.05-0.69% using Ni/ZSM-5 based catalysts, and 0.06-0.078% using Ni/SAPO-11 based catalysts in case of batch reactor sourced pyrolysis oils; or 0.003-0.005% for the Ni/ZSM-5 catalysts and 0.004-0.007% for Ni/SAPO-11 catalysts, in case of the tubular reactor. It means that the catalysts can be reduced the amount of the separated fraction. By comparing the two catalyst supporters, it can be said that in all cases the catalyst mixtures containing Ni/SAPO-11 showed higher values. This is most likely

due to the higher branched hydrocarbon content of pyrolysis oils produced by ZSM-5 zeolite since they have less activity in the formation of larger fragments, which can be filtered. On the other hand, the difference also can be attributed to the difference in the distribution of the hydrocarbon structure of unsaturated compounds [276,277].

Owing to the insolubility in the light oil matrix of the larger oligomer-polymer molecules (molecule-agglomerates) with higher molecular weight, the solid deposition was suggested based on the density and viscosity results. To conclude results, it is clear that the formation of those large macromolecules was without the notable production of light oil-soluble smaller molecule-agglomerates. This is the reason why the density and viscosity did not increase to such an extent that the amount of oligomer-polymer molecules on the filter. Regarding the product utilization, the molecule agglomerates could lead to phase separation or the plugging of the filters, which is non-favored for storage, transportation of waste-derived fuels. Consequently, the use of catalysts, especially with high Ni/ZSM-5 and Ni/SAPO-11 content had a significant advantage for further fuel-like application of the light oils [276,277].

To investigate the acidic property of the light oils TAN measurement was carried out and the results are summarized in **Figure 3.19**. It is well known, those corrosion problems could be caused by the chlorine-containing compounds. The light oil obtained in the catalyst-free case using a tubular reactor has a higher acidity (TAN =11.5) than that of in case of batch reactor sourced pyrolysis oil (5.9 mgKOH/g sample). The TAN of the catalyst-free sourced liquid fractions increase by 70% (to 19.4mgKOH/g sample) (batch reactor) and 19% (to 14.4mgKOH/g sample) (tubular reactor). Presumably, acidic chlorine-containing compounds can be transformed from the chlorinated organic components during the aging. The increase in TAN was less using catalysts, especially in the case of SAPO-11. E.g. in case of the batch reactor the TAN can be increased with 36-57% and 29-48% using Ni/ZSM-5 and Ni/SAPO-11 containing catalysts, respectively. In case of catalytic pyrolysis product from tubular reactor, the change in TAN was in the range of 14-17% (Ni/ZSM-5 based catalysts) and 9-14% (Ni/SAPO-11 based catalysts). It is also well presented that ZSM-5 catalyst had lower efficiency in reducing the amount of acid components. To conclude the effect of the catalysts, it is also clear than the total acid number of light oil produced on catalysts with large amounts of alkaline components have been changed the least [276,277].



**Figure 3.19**  
Total Acid Number of the liquid fractions after the aging test

### 3.3.4. Main conclusions of chlorinated plastic pyrolysis

It was concluded, that the catalyst mixtures can increase the yields of volatiles, especially catalysts with high synthetic zeolite content. Comparing to Ni/SAPO-11, due to the larger microporous surface area, strong acidity and wider average pores of the catalyst, ZSM-5 can lead to more significant decomposition of C-C bonds. Red mud can promote the hydrogen production, however, the isomerization effect of Ni/ZSM-5 based catalysts were more significant, than that of Ni/SAPO-11 based. Gases contain chloromethane and chloroethane as organic chlorinated hydrocarbons and the Ni/SAPO-11 based catalysts showed advanced properties for de-chlorination especially due to HCl formation which led also to significant reduction in the chlorine content of the light oil. However, due to

the sorption properties of the catalysts, the chlorine content of the solid residue can increase. Catalysts with high red mud and/or  $\text{Ca}(\text{OH})_2$  content showed high activity in chlorine reduction. Comparing the two reactors, gases and light oil obtained by tubular reactor had higher chlorine content, than that of batch reactor. As a result of the higher catalyst activity and longer residence time, the concentration of aromatics was higher using a batch reactor, comparing to the tubular reactor. Using of Ni/ZSM-5 catalyst, the multi-rings aromatics was dominant in pyrolysis oils, while the single-ring aromatic in case of Ni/SAPO-11 catalysts. From another point of view, the smaller pore size of Ni/SAPO-11 limits the diffusion of molecules which results in lower aromatic concentration. Ni/SAPO-11 and Ni/ZSM-5 based catalyst has exhibited an advanced capability for carbon frame isomerization which increase considerably the yield of branched hydrocarbon and decreased the yield of n-olefin and n-paraffin. More aromatic and less branched hydrocarbons were found in pyrolysis oils using a batch reactor system. Meanwhile, the use of Ni/SAPO-11 based catalysts has resulted in lower n-paraffin/n-olefin ratios than Ni/ZSM-5 based.

The thermal pyrolysis process using both batch and tubular reactor reactors has produced an oil with a higher aging increasing rate. Conversely, the catalysts had a beneficial effect on suppressing the aging process. It was also concluded, that the density and viscosity change was slightly during the aging test, and small amount of the residues can be filtered from the light oil. In general, light oil from tubular reactor had better properties, than that of from batch reactor (less solid deposition and lower TAN). Corrosion test shows, that Ni/SAPO-11 catalysts (especially with high red mud and  $\text{Ca}(\text{OH})_2$  content) also had a positive effect on long-term applicability of the light oils.

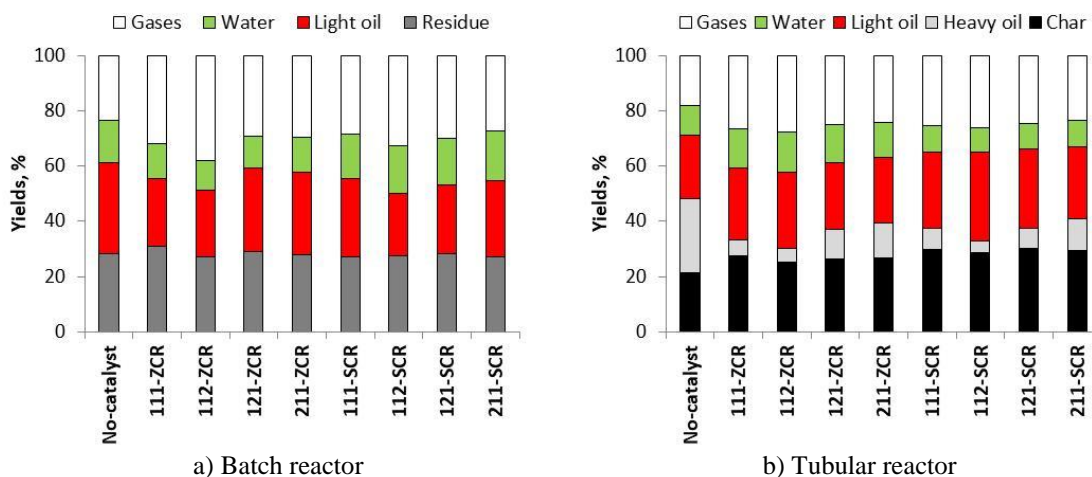
Regarding the heavy oil physical and chemical characteristics, the introduction of the catalysts has reduced the density, viscosity, melting point, and the flash point. Conversely, concerning the HHV, no significant difference was established by the catalyst use.

### **3.4. Pyrolysis of newspaper, cardboard and plastic**

It is well known, that the many compounds containing oxygen are obtained by the pyrolysis of cellulose, which can deteriorate the pyrolysis oil properties. In this chapter, the pyrolysis of real waste plastic containing paper (newspaper and cardboard) and the longer-term utilization of pyrolysis oils are investigated.

### 3.4.1. Product yields

The yields of products obtained by batch and tubular reactors are summarized in *Figure 3.20*. Results well showed, that not only the used catalysts but also the reactor construction have a key role in the pyrolysis reactions because the higher gas yield was found using a batch reactor. However, no significant change was found in the amount of solid char. The light oil yield decreased in the case of a batch reactor, while that of increased in case of the tubular process by the use of catalysts. It is important to mention, regarding the batch reactor, the pyrolysis reaction was carried out until no vapors come out from the operation unit. Therefore no heavy oil was formed in case of the batch process because that fraction was totally decomposed. To investigate the effect of the catalysts, due to the before mentioned specialty of the batch reactor, lower yield of light oil was found in the presence of catalysts compared to the catalyst-free case in case of batch pyrolysis. Especially using Ni/ZSM-5 based catalysts mixtures. The light oil yield was 22.6% without catalysts. Regarding the effect of the operation unit, the yield of light oil was slightly higher using a tubular reactor with Ni/ZSM-5 and Ni/SAPO-11 based catalysts, because it was in the range of 23.8-27.3% and 26.1-32.1 %, respectively. However, the gas yield can significantly be increased, while the heavy oil yield can be decreased by catalysts [288].



**Figure 3.20**  
The yields of pyrolysis products

The composition of the catalysts can also affect the yield of solid fraction. An only a slight difference was found in case of batch pyrolysis, however, a significant effect of the catalysts to the solid fraction was concluded in case of the tubular system. The yield of

the solid fraction was a bit higher in case of Ni/ZSM-5 catalysts mixtures than Ni/SAPO-11 based using the batch reactor, however, significantly more char was found in case of Ni/SAPO-11 based catalysts than in case of Ni/ZSM-5 based catalysts using tubular reactor. However, it should be noted that the increase compared to the thermal case was primarily due to the catalyst incorporated into the feedstock because it was accumulated in this fraction.

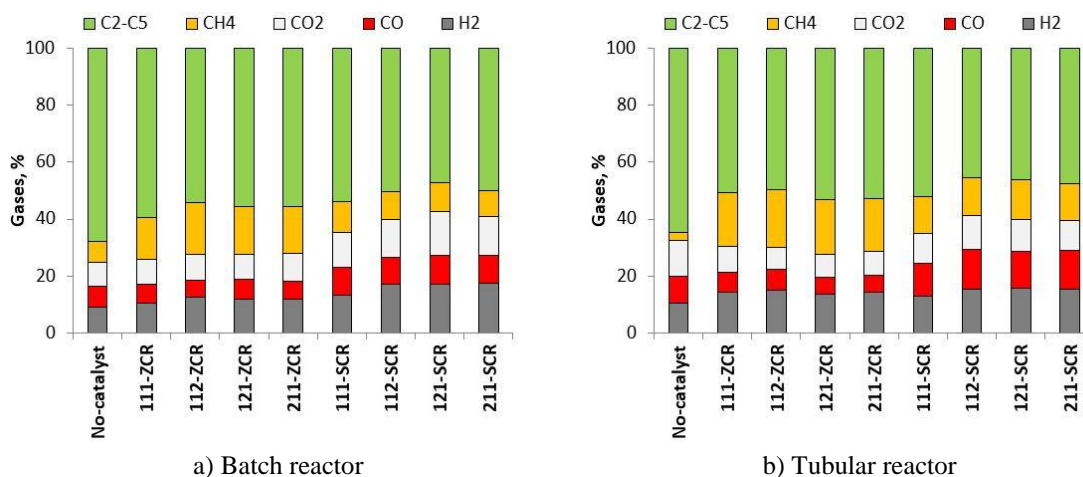
Due to the presence of newspaper and cardboard, liquid products contain water, which can be separated from the hydrocarbon oil. It is important to mention, that the catalysts can increase the water yield, especially Ni/ZSM-5 based catalysts in a tubular reactor and Ni/SAPO-11 based catalysts using batch reactor. Catalysts can also increase the gas yield, mainly due to the enhancement of the faster cracking of C-C bonds on catalyst active sites. On the other hand, not only the catalyst presence but also the reactor type has a significant effect to the gas yield, because the yield of gas products was considerably higher by the using of the batch reactor (23.3% (batch reactor) and 18.2% (tubular reactor) without catalysts). It is an important observation, that the Ni/ZSM-5 based catalysts had higher activity in gas production in case of both types of the reactors than Ni/SAPO-11 based, which was caused by the higher surface area and higher Si/Al ratio of the Ni/ZSM-5 zeolite. Especially catalysts with high synthetic zeolite content can increase significantly the gas yield (112-ZSM-5 and 112-SAPO-11) [288].

### **3.4.2. Products properties**

#### **3.4.2.1. Gases**

The composition of gases obtained from the batch and tubular process is summarized in **Figure 3.21**. In contrast with the result obtained by the pyrolysis of chlorinated raw materials (**Chapter 3.2**), not only hydrocarbons but also CO and CO<sub>2</sub> should be also identified in the gas products, which was the consequence of the cellulose content in the newspaper and cardboard. The CO<sub>2</sub> production can cause environmental and sustainable problems, because of the limited emission of CO<sub>2</sub> into the atmosphere. Comparing the batch and tubular reactors, and the effect of the catalysts, 10.5% hydrogen, 9.3% CO, 12.5% CO<sub>2</sub>, 2.8% methane and 64.9% C<sub>2</sub>-C<sub>5</sub> hydrocarbon was found using tubular reactor. Furthermore, the following composition of gases was concluded in the case of batch pyrolysis: 8.9% hydrogen, 7.3% CO, 8.4% CO<sub>2</sub>, 7.4% methane and 68.0% other hydrocarbons up to C<sub>5</sub>. Regarding the CO and CO<sub>2</sub>, in the case of thermo-catalytic pyrolysis using

Ni/SAPO-11 based catalysts, higher CO<sub>2</sub> concentration was found in a batch reactor, than tubular. On the other hand, slightly higher CO was detected by the use of a tubular reactor than a batch reactor. It is important to mention, that the yield of carbon monoxide can be only slightly increased by catalysts. The concentration of CO was in the range of 5.8-7.4% over Ni/ZSM-5 based catalysts and between 11.6 and 14.2% by the use of Ni/SAPO-11 based catalyst mixture in case of the tubular reactor [288].



**Figure 3.21**  
The composition of gases

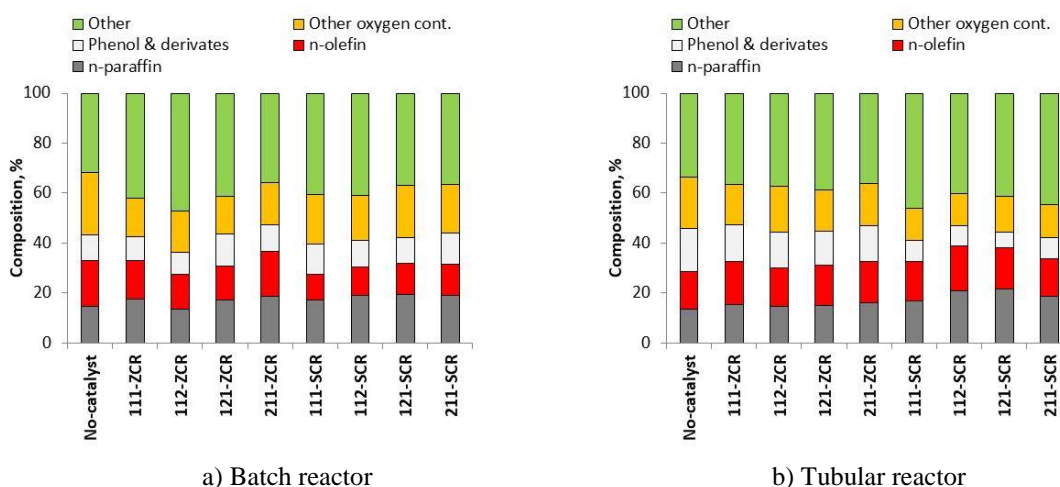
Results also show that higher methane concentration was found in the batch process than in tubular without the catalyst. Ni/ZSM-5 catalysts can significantly increase the methane content, which was the consequence of the C-C cracking activity of the synthetic zeolite. E.g. the methane concentration was in the range of 18.5-20.3% and 12.7-14.2% in the presence of Ni/ZSM-5 and Ni/SAPO-11 based catalysts, respectively.

It is also clear, that the tubular reactor is beneficial construction for hydrogen production because higher hydrogen yield was found in case of both thermal pyrolysis (10.5%) and in case of thermo-catalytic pyrolysis using Ni/ZSM-5 based catalysts (13.7-14.9%) than the batch reactor. On the contrary, a bit higher hydrogen yield was obtained in a batch reactor using Ni/SAPO-11 based catalysts (13.3-17.3%), comparing to the tubular reactor (12.9-15.7%). For chemically viewing point, due to the possibility for in-situ hydrogenation, the hydrogen has rather positive effect to the pyrolysis products. Regarding the C<sub>2</sub>-C<sub>5</sub> hydrocarbons, catalysts can decrease the yields from 68% (batch process) or 64.9% (tubular process) to 47.1-62.3% (batch process) and 45.3-53.2% (tubular process).

Furthermore, Ni/ZSM-5 based catalysts resulted in more hydrocarbons in gases both in batch and tubular reactors [288].

### 3.4.2.2. Light oil

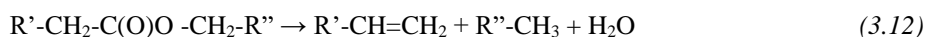
The compositions of light oils are summarized in **Figures 3.22**. Results well showed that the liquid fraction of the pyrolysis contained n-paraffin; n-olefin; phenol and its derivatives and other oxygen-containing compounds (aldehydes; carboxylic acid and ketones) in case of both batch and tubular processes, which is significantly different results comparing the light oil composition obtained by the pyrolysis of chlorinated waste (**Chapter 3.2**). One of the main results for longer-term utilization of the light oils, that each catalyst can significantly affect the amount of compounds containing oxygen. On the other hand, not only the catalyst presence but also the reactor configuration has an important role regarding the compounds containing oxygen. E.g. the yield of phenolic compounds was considerably higher using a tubular reactor without catalysts. It was 10.3% and 17.4% using the batch process and tubular reactor, respectively. Regarding the effect of the catalysts on the phenolic compounds, it is clear, that Ni/ZSM-5 based catalyst mixtures can reduce that in the case of both reactors. However, the Ni/SAPO-11 based catalyst mixtures had resulted in a higher yield of phenolic compounds in the case of batch pyrolysis. Furthermore, those catalysts have higher efficiency in the transformation of phenolic compounds in the tubular reactor, because their concentration decreased to the range of 6.2-8.5% [288].



**Figure 3.22**  
The composition of light oils

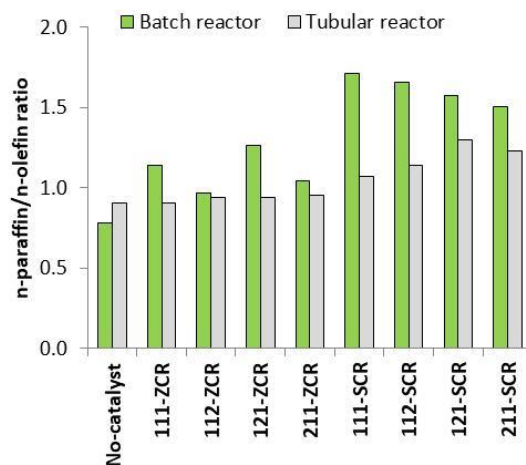


Results also have shown, that 24.8% (batch process) and 20.5% (tubular reactor) oxygenated compounds were found (without phenol and its derivatives) in catalyst-free pyrolysis, which can significantly be reduced by catalysts. E.g. to the range of 15.0%-16.9% (Ni/ZSM-5 based catalysts) and 17.9%-20.7% (Ni/SAPO-11 based catalyst) using the batch reactor, or even to 16.2-18.4% (Ni/ZSM-5 based catalysts) and 12.8-14.2% (Ni/SAPO-11 based catalyst) using tubular reactor. The possible reaction scheme responsible for decreasing in oxygen-containing compounds is summarized in (3.10-3.12). On one hand, the oxygen-containing compounds can be transformed to n-olefin, n-paraffin and aromatics free from -OH and -COOH groups, while the functional groups with oxygen can transform into water.



Light oil contained 18.6% and 15.0% n-olefin in the case of batch and tubular process without catalysts, respectively. It is a strange result, that the catalysts can decrease the n-olefin content in the batch process, while the opposite tendency was found in the case of a tubular reactor comparing that to the catalyst-free case. It is also clear, that of the concentration of n-olefin was higher in the case of catalytic pyrolysis in a tubular reactor comparing that of to the batch reactor [288].

The n-paraffin and n-olefin ratios of the liquid products were shown in **Figure 3.23**. In the case of thermo-catalytic pyrolysis higher n-paraffin/n-olefin ratio was found by using the batch reactor, than in tubular. On the other hand, the n-paraffin and n-olefin ratio can increase by catalysts independently from the reactor configuration and the catalyst to be used. E.g. the n-paraffin/n-olefin ratio changed 0.78  $\rightarrow$  0.97-1.26 (Ni/ZSM-5 based catalysts) and 0.78  $\rightarrow$  1.50-1.71 (Ni/SAPO-11 based catalysts) using batch reactor; or 0.90  $\rightarrow$  0.91-0.95 (Ni/ZSM-5 based catalysts) and 0.90  $\rightarrow$  1.10-1.29 (Ni/SAPO-11 based catalysts) using tubular reactor. The higher activity of the SAPO-11 catalyst in saturation reaction should be blamed by the higher hydrogen concentration in the gas products (**Figure 3.21**).



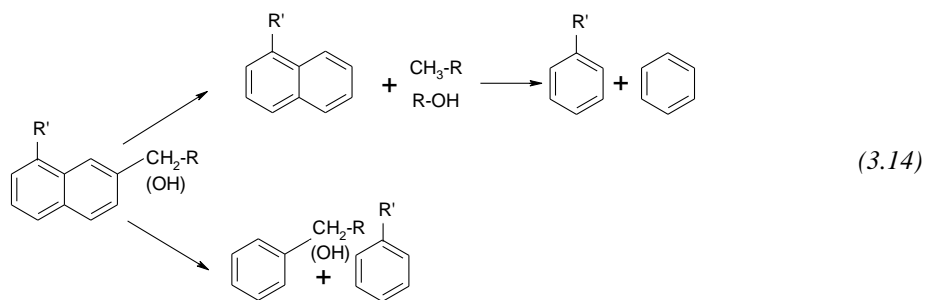
**Figure 3.23**  
The n-paraffin/n-olefin ratio of light oils

It is also known, that the saturation reactions are promoted by the active sites of the Ni-containing catalyst. Presumably, the in-situ saturation of the n-olefins that occurred by the partial hydrogen excess generated by the cracking of raw material was the cause of the increase in n-paraffin/n-olefin ratio (3.13). Furthermore, the more efficient saturation can be caused by the longer reaction time in the case of batch pyrolysis [288].

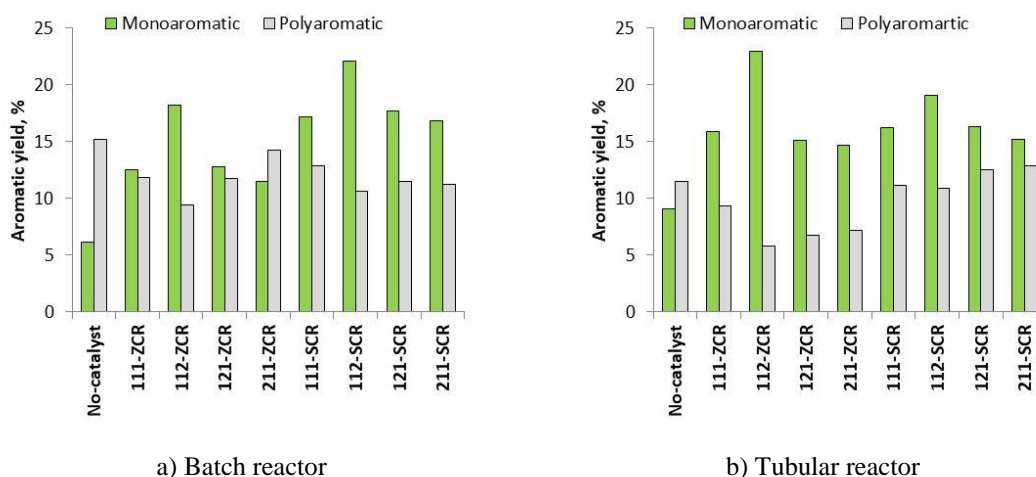


The concentration of aromatic hydrocarbons is summarized in **Figure 3.24**, which well shown that monoaromatic and polyaromatic hydrocarbons were found in the liquid fractions of the pyrolysis. Similarly, as it was earlier demonstrated (**Figure 3.12**) catalysts had a significant effect on the aromatization reactions, e.g. the concentration of single ring aromatics was increased, while mostly less polyaromatic hydrocarbons were found by catalysts. Especially the 112-ZCR and 112-SCR signed catalysts can increase significantly the yield of monoaromatic hydrocarbons. Presumably, the polyaromatics can further be cracked into monoaromatic compounds in the presence of catalysts (3.14).

Furthermore, a higher summarized yield of aromatics was also found in the presence of catalysts, which shows that not only the conversions of the polyaromatics into monoaromatics but also the aromatization reactions have occurred over catalysts; especially by the using of 112-ZCR and 112-SCR catalyst mixtures. It is also clear, that ZSM-5 had high activity in aromatization reactions during the waste polymer pyrolysis [288].



Comparing the two reactors, no significant difference in the total aromatic content was concluded: 21.3-32.7% (batch process) and 20.3-30.0% (tubular reactor). However, a higher concentration of mono-aromatics was found in the case of the tubular reactor and more polyaromatic hydrocarbons in case of the batch reactor using Ni/ZSM-5 based catalyst mixtures. In contrast, the concentration of both mono-aromatic and polyaromatic were slightly lower in case of a tubular reactor compared to the batch process using Ni/SAPO-11 based catalyst mixtures [288].



**Figure 3.24**  
The aromatic content of light oils

The main properties of the light oils are summarized in **Table 3.6**. The density and viscosity changed in the range of 0.718-0.812 g/cm<sup>3</sup> and 1.722-2.371mm<sup>2</sup>/s respectively. The flash point was below 50°C. The colour of the light oil obtained by batch reactor was dark brown/black, while that of from tubular reactor yellowish. The TAN was under 20 mgKOH/g sample in each case, however liquid fractions with lower acidity can be obtained from from tubular reactor.

**Table 3.6**  
Main properties of light oils obtained by pyrolysis of chlorinated waste plastics

		No-cat- alyst	111- ZCR	112- ZCR	121- ZCR	211- ZCR	111- SCR	112- SCR	121- SCR	211- SCR
Batch reactor	Colour	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown
	Density, g/cm <sup>3</sup> (at 20°C)	0.812	0.767	0.738	0.747	0.755	0.778	0.755	0.767	0.771
	Viscosity, mm <sup>2</sup> /s (at 20°C)	2.371	2.115	1.957	2.218	2.193	2.209	2.105	2.221	2.229
	Flash point, °C	<50	<50	<50	<50	<50	<50	<50	<50	<50
	TAN, mgKOH/g	19.7	11.5	12.8	11.9	12.4	14.8	15.3	14.2	14.9
Tubular reactor	Colour	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish	Yel- lowish
	Density, g/cm <sup>3</sup> (at 20°C)	0.796	0.755	0.718	0.738	0.729	0.768	0.739	0.758	0.742
	Viscosity, mm <sup>2</sup> /s (at 20°C)	2.185	2.007	1.722	1.894	1.948	1.942	1.836	1.925	1.953
	Flash point, °C	<50	<50	<50	<50	<50	<50	<50	<50	<50
	TAN, mgKOH/g	15.2	10.8	10.3	11.2	10.7	9.1	8.3	7.3	8.9

### 3.4.2.3. Heavy oil

The main characteristics of the heavy oil obtained by the pyrolysis of waste plastics containing paper in tubular reactor are summarized in **Table 3.7**. The heavy oils have black colour and they were grease-like as it was mentioned in the *subchapter 3.2.2.3*.

**Table 3.7**  
Main properties of heavy oils obtained by pyrolysis of waste plastic containing paper

	No-catalyst	111- ZCR	112- ZCR	121- ZCR	211- ZCR	111- SCR	112- SCR	121- SCR	211- SCR
Density, g/cm <sup>3</sup> (at 100°C)	0.861	0.832	0.809	0.854	0.842	0.833	0.825	0.842	0.835
Viscosity, mm <sup>2</sup> /s (at 100°C)	6.92	5.81	5.15	6.12	5.79	5.56	5.29	5.51	5.26
Melting point, °C	88	79	79	81	82	80	80	81	84
Flash point, °C	218	202	197	205	209	208	210	209	210
IBP, °C	145	141	140	137	139	139	142	138	139
FBP, °C	>350	>350	>350	>350	>350	>350	>350	>350	>350
Caloric value, MJ/kg	41.1	41.5	41.2	41.1	41.3	41.1	41.2	40.2	41.3

As it was found for the products obtained from the cracking of chlorine-containing plastic waste, the presence of catalysts can reduce the density, viscosity, melting point, and flash point. The density of heavy oil produced by cracking waste plastic containing paper was higher in each case than that of heavy oil obtained by pyrolysis of chlorine-containing plastic waste. Similar results were also obtained for the viscosity measured at 100°C. At the same time, the freezing point and flash point were lower for heavy oil obtained by the pyrolysis of waste plastic containing paper. It is worth mentioning that for each listed property the lowest values were obtained by the using of the 112-ZCR and

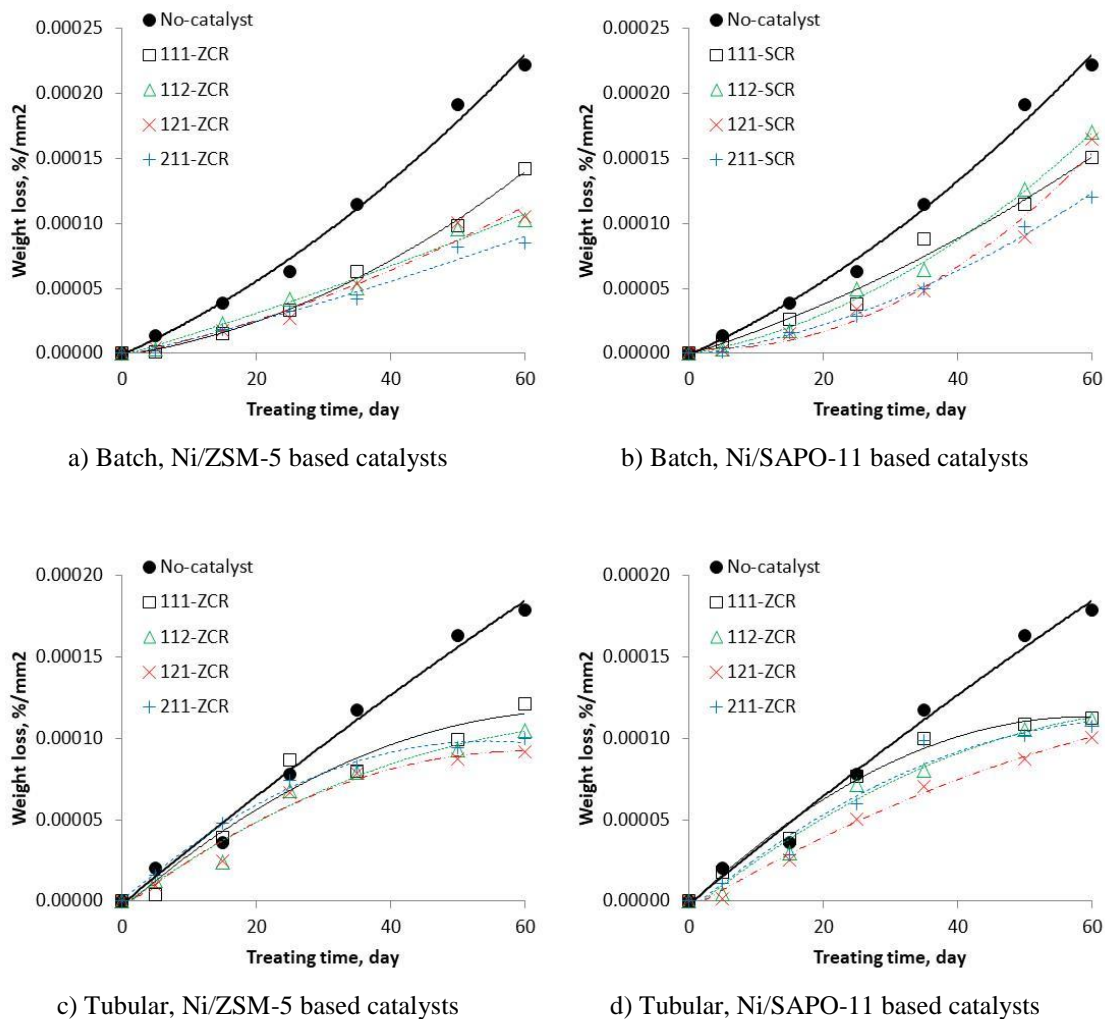
112 catalysts. This was mainly due to the significant cracking effect of both zeolite catalysts. Comparing the two different types of catalysts, it is also clear that ZSM-5-based catalysts had higher densities and viscosities and lower melting points and flash points than SAPO-11-based catalysts.

As a result of the use of the catalysts, the initial boiling point of the heavy oil product decreased slightly, which was due to the isomerizing effect of the catalyst. This was more significant for SAPO-11 based catalysts than that of in case of ZSM-5 based catalysts. In the case of HHV values, not tendentious change was found under the influence of catalysts. They can differ only slightly from the HHV values of heavy oil produced by the pyrolysis of chlorine-containing plastic waste.

### **3.4.3. Longer-term properties of pyrolysis oils**

#### **3.4.3.1. Corrosion test**

*Figure 3.25* summarizes the outcomes of the copper plate corrosion tests of the light oils. Results well showed that the weight of the copper plate decreased as a function of the test time. On the 60<sup>th</sup> day of the treating, the weight loss of the copper plate was 0.00017% in case of hydrocarbons obtained by the tubular reactor and 0.00022% by using the light oil produced from batch reactor without catalysts. The highest weight loss was found in case of thermal pyrolysis sourced oils. However, less reduction in weight loss was observed in all types of catalytic pyrolysis. Nevertheless, a slight difference in the effect of catalysts on the plat weight loss was identified. Under all circumstances, the best results (less weight loss) were achieved over "121-Z, 211-Z, 121-S and 211-S catalysts. Regarding the comparison of the reactor configuration, it is clear, that the tubular reactor has produced light oil with more advantageous corrosion properties. By using the batch reactor and in either catalytic or thermal pyrolysis cases the degree of weight loss was exponential. Conversely, in case of the tubular process, a flattening curve of copper plate weight loss was identified in the case of catalytic pyrolysis, while in case of thermal pyrolysis has a linear tendency [288].



**Figure 3.25**  
Weight loss of the copper plate sample during the corrosion test

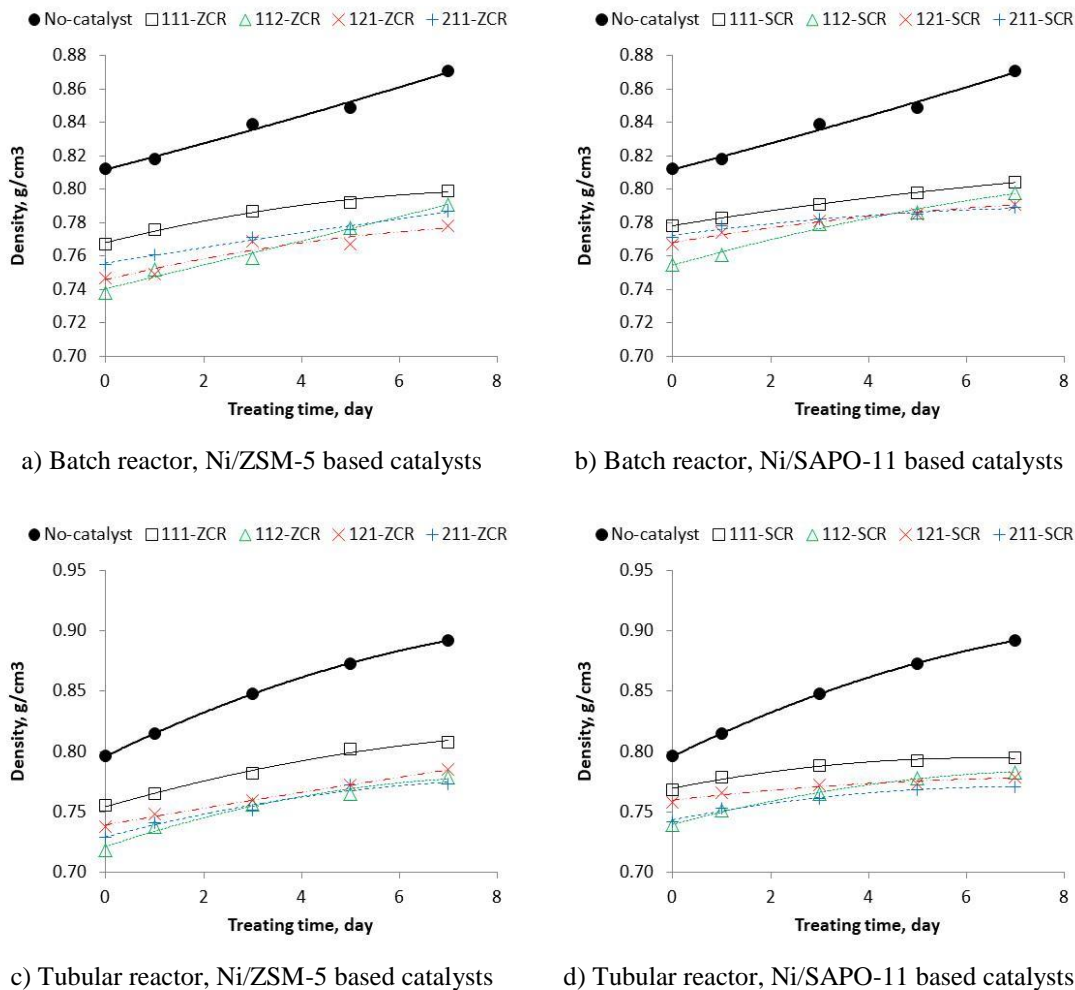
Comparing the result with the weight loss of copper plate occurred by polyolefin containing PVC waste sourced light oil, less change was found using polyolefin containing paper raw materials [276,277]. On one hand, the plastic wastes containing PVC produced light oils had a higher weight loss of the copper plate because it was around 1000 times higher (with a maximum of 0.6-0.7). That significant difference was occurred by the presence of organochlorine compounds, which could increase the weight loss substantially. However, the oxygen-containing compounds such as carboxylic acids, alcohols, aldehydes and ketones had a considerably lower destructive effect on the structural material. E.g. the weight loss at the 60<sup>th</sup> day was 51.5-61.8% (Ni/ZSM-5 based catalyst mixtures) and 56.4-62.9% (Ni/SAPO-11 based catalyst mixtures) compared to the weight loss in case of the non-catalytic pyrolysis using batch reactor. Regarding the light oil from the

tubular reactor, the weight loss was 38.3-63.9% (Ni/ZSM-5 based catalyst mixtures) and 54.0-76.1% (Ni/SAPO-11 based catalyst mixtures).

#### **3.4.3.2. Accelerated aging test**

The density and viscosity of the light oils were summarized in **Figures 3.26 and 3.27**. Results well show, that similarly, as it was mentioned in **Chapter 3.2.3.2**, higher density and viscosity was obtained by catalyst free thermal pyrolysis in both reactor configurations (tubular and batch). On the other hand, both properties were increased as a function of treating time. The density of the light oil was 0.812g/cm<sup>3</sup> (batch reactor) and 0.796g/cm<sup>3</sup> (tubular reactor) without catalysts, which can be increased by 7.3% and 12.1%, respectively. It means, that a higher increase in density was found in case of tubular reactor sourced light oil. Not only the density but also the viscosity of the light oil was also higher without catalysts, comparing that of with thermo-catalytic case. The viscosity of the light oil obtained by catalyst-free pyrolysis was 2.371mm<sup>2</sup>/s (batch reactor) and 2.185mm<sup>2</sup>/s (tubular reactor). However, less difference was found in the increase rate between the two reactor configurations, because the viscosity can increase by 10.8% (batch reactor) and 10.4% (tubular reactor) at the 7<sup>th</sup> day of the aging compared to the initial value. It is important to remark, that both without and with catalysts higher viscosity and lower density were found in case of polyolefin containing paper derived light oil, than that of using chlorinated raw material (**Chapter 3.2**).

The viscosity and density of the produced oil can be decreased by catalysts. E.g. the density changed to 0.738-0.778g/cm<sup>3</sup> (batch reactor) and 0.729g/cm<sup>3</sup>-0.768g/m<sup>3</sup> (tubular reactor) depending on the used catalysts. On the other hand, a slightly lower change in the density and viscosity was found during the aging test of the pyrolysis oils produced by batch reactor than that of the tubular reactor. However, it should be pointed out that those differences were not significant. Comparing the different catalysts mixtures, it can be concluded, that their high synthetic zeolite content (112-ZCR and 112-SCR) can reduce both the density and viscosity in the highest degree. This is a similar observation, as it was found using chlorinated raw materials (**Chapter 3.2**), which is favorable for further utilization (e.g. better flow properties) [288].

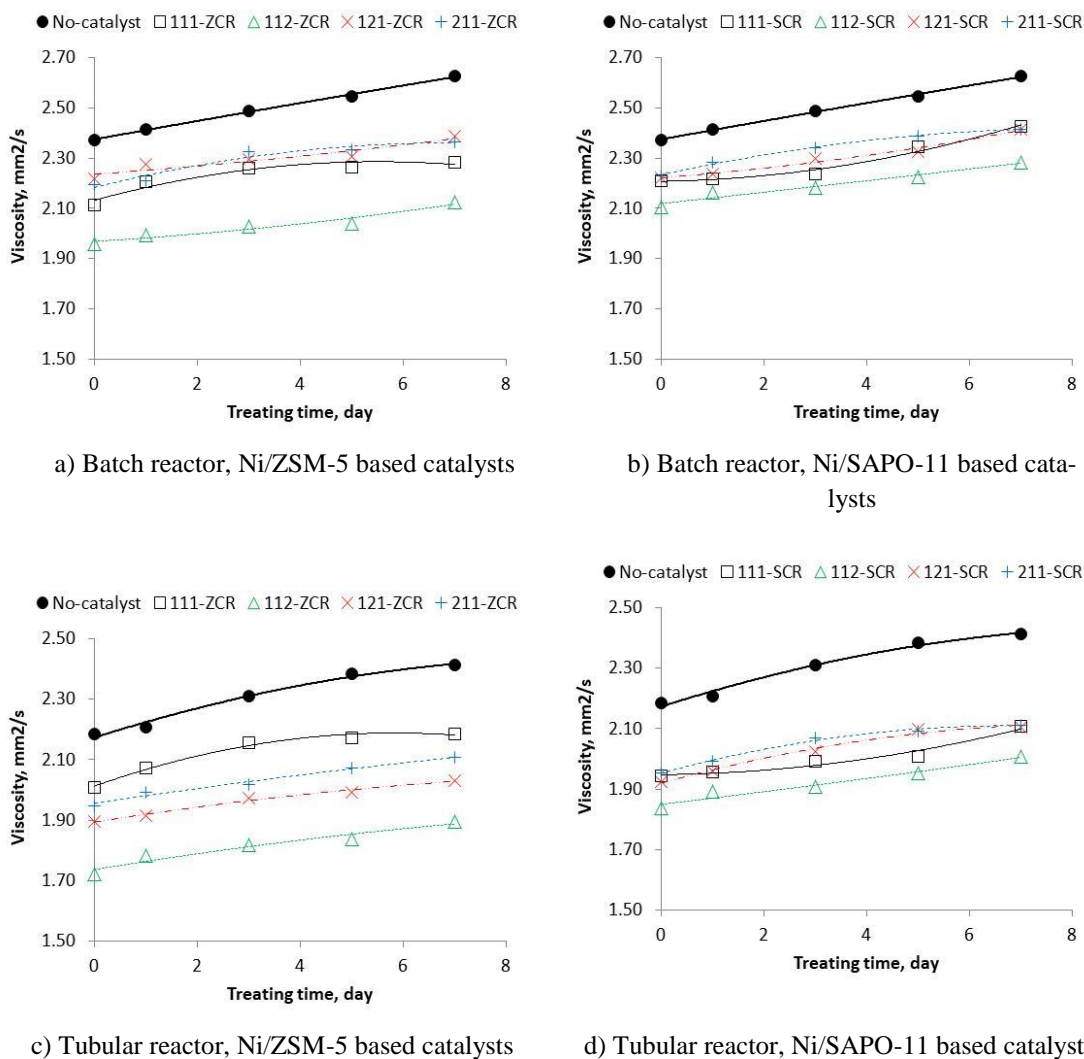


**Figure 3.26**  
The density of pyrolysis oils during the aging test

Contrary, those fractions (light oils from pyrolysis over 112-ZCR and 112-SCR catalysts) showed the worst property during the aging (higher increase in both density and viscosity). Furthermore, a higher increase in both properties was also demonstrated using a tubular reactor. E.g. the change in the density was in the range of 2.3-7.2% (batch reactor) and 2.8-8.5% (tubular reactor), while the viscosity can be increased by 7.2-9.8% (batch reactor) and 7.7-10.0% (tubular reactor). The use of catalysts mixtures with high alkali ( $\text{Ca}(\text{OH})_2$  or red mud) content (121-ZCR, 121-SCR, 211-ZCR and 211-SCR) resulted in the less increase in both density and viscosity, which was found in case of both tubular and batch reactors. This phenomenon can be attributed to the outcomes of the composition differences of the pyrolysis oils. As it was before mentioned, that less reactive chemical compounds such as aldehyde, ketone, carboxylic acid, etc., were concluded in case of pyrolysis over alkaline-rich catalysts. Therefore those fractions can be slightly



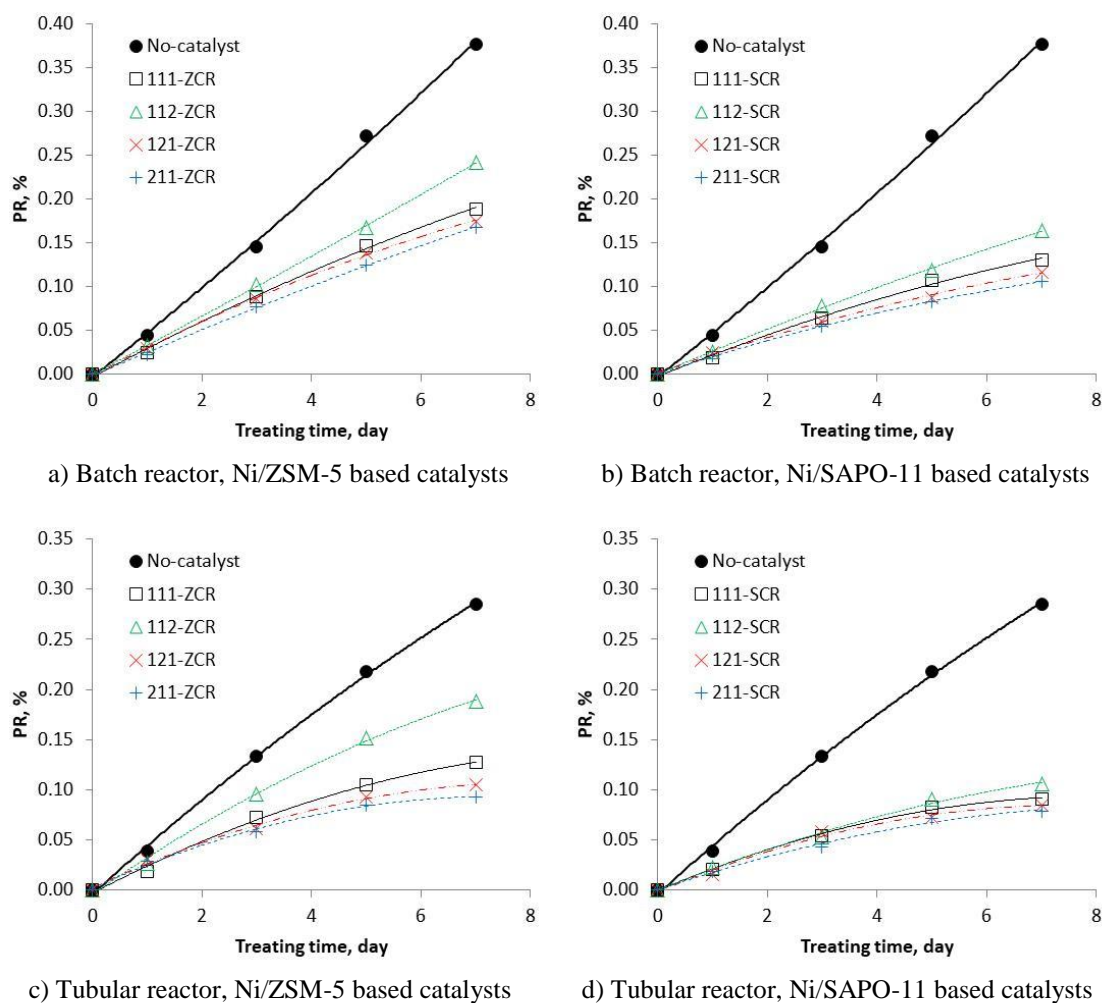
agglomerated into larger molecules during the aging. These and previous results (*Chapter 3.2.3.2*) suggest that oxygen-containing compounds are more important than chlorinated derivatives in increasing the density and viscosity of aging. The latter can increase both properties only by significantly less percentage during the aging test [288].



**Figure 3.27**  
The viscosity of pyrolysis oils during the aging test

The amount of solid polymeric depositions, which could be filtered from the light oil are shown in *Figure 3.28*. Similar to the results presented above, the amount of depositions significantly increased as a function of the aging time in all cases. It is worth mentioning that without catalyst and by using the batch reactor, more deposition was achieved in the filter after the 7<sup>th</sup> day of the treating. It is well shown, that the advantageous properties of the catalysts were also the reduction in the amount of solid deposition. At the same time, there was a notable increase in the solid deposition in case of waste plastic-

paper derived light oil, compared to that of light oil fractions obtained from the polyolefin-PVC feedstock. It can also be said that for the polyolefin-paper waste feedstock there were significantly smaller differences in the solid deposition values regarding the light oil samples from the batch and tubular reactors. However, the aging of the light oils obtained in the tubular reactor was also more favorable [288].

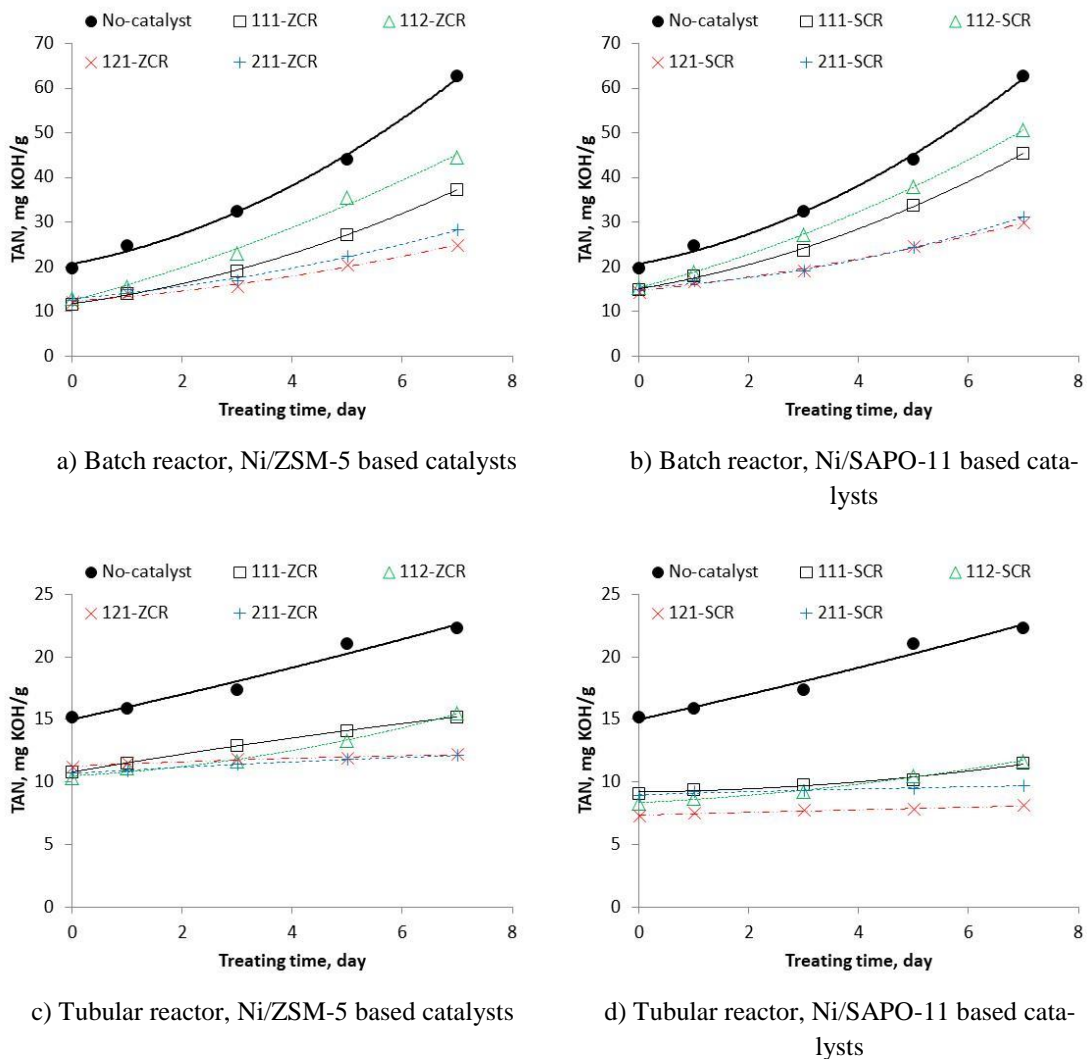


**Figure 3.28**  
Polymer-oligomer residue on the filter after the aging test

The catalyst presence is advantageous because it produces a light oil that shows drastically less increasing in terms of solid polymeric depositions. Correspondingly, the 112-ZCR and 112-SCR catalysts exhibited the worst properties as a consequence of the high content of oxygenated acidic compounds that can react with each other, which can lead to the formation of larger molecules agglomerates. In contrast, a higher alkali content catalyst has reduced the solids depositions more efficiently in the case of accelerated aging. Based on the above results, it can be seen that the high synthetic zeolite-containing

catalysts had a significant effect on the reactions of C-C bond cracking and isomerization, while the alkaline components showed more favorable properties in the neutralization of acidic components and in long-term properties. The amount of the solid deposition was 0.377% (batch process) and 0.285% (tubular process) at the 7<sup>th</sup> day of the treating, which can be reduced to 0.106-0.242% (batch process) and 0.079-0.188% (tubular process) by the using of catalysts. On the other hand, presumably due to the less acidic character of the catalyst, lower values and higher efficiency in the reduction was found over Ni/SAPO-11 based catalyst mixtures. Regarding the catalyst efficiency for the reduction of solid deposition, no significant effect of the reactor configuration was concluded, because the change was in the range of 35.8-71.8% (batch reactor) and 34.0-72.3% (tubular reactor).

The TAN of the samples are summarized in *Figure 3.29*. The pyrolysis oils have relatively high TAN values (15.2 mgKOH/g (tubular process) and 19.7 mgKOH/g (batch reactor)). These values, depending on the parameters used, are nearly three to eight times higher than those observed during the aging of light oils obtained from chlorinated raw material. It should also be noted that not only the values of TAN but also their rate of growth were significantly higher than those of chlorinated feedstocks. In the absence of a catalyst, the TAN increase was 68.6% on the 7<sup>th</sup> day in case of the batch reactor and 31.8% using a tubular reactor. In contrast, the hydrocarbon fractions obtained by the cracking of chlorinated feedstock had 50.9% (batch reactor) and 18.4% (tubular reactor) TAN increasing. In the case of a batch reactor, no significant decrease in the tendency was observed with the use of catalysts, since the growth rate ranged from 52.1 to 71.3%. The use of catalysts showed a more significant decrease of TAN in the tubular reactor because the change was between 8.2-33.5%. As was previously found, the high alkali content catalysts showed better properties for the elimination of disadvantageous property of the hydrocarbons containing oxygen. Due to aging, these catalysts (121-ZCR, 121-SCR, 211-ZCR and 211-SCR) resulted in the TAN increase of 52.1-56.0% (batch reactor) and 8.2-11.6% (tubular reactor), which is considerably lower, than that of in case of catalyst-free thermal pyrolysis, or even result obtained by the using of 111-ZCR, 112-ZCR, 111-SCR or 112-SCR marked catalysts [288].



**Figure 3.29**  
Total Acid Number of the liquid fractions after the aging test

### 3.4.4. Main conclusions of paper and plastic pyrolysis

Based on the results of co-pyrolysis of paper and plastics was concluded, that the catalysts can significantly increase the yield of volatiles and improve product properties. Water and a wide range of oxygenated compounds was found in the liquid product due to the newspaper and cardboard in the raw materials. However, the yield of water can not be significantly affected by the catalysts. The Ni/ZSM-5 based catalysts had higher activity in gas production in case of both types of the reactors than Ni/SAPO-11 based. CO and CO<sub>2</sub> should be also found in the gas products, which was the consequence of the cellulose content in the newspaper and cardboard. Regarding the gas fraction, slightly higher CO was identified through the use of a tubular reactor than a batch reactor, while

the catalysts can promote the yield of hydrogen and methane and decrease the CO<sub>2</sub> content using tubular reactor. With regard to the oxygenated compounds, it can significantly be reduced by catalysts where the functional groups with oxygen can transform into water and Ni/ZSM-5 based catalyst mixtures can reduce the phenolic compounds in the case of both reactors. The catalysts can decrease the n-olefin content in the batch process, while the opposite tendency was found in the case of a tubular reactor comparing that to the catalyst-free case.

In the matter of heavy oil composition, the presence of catalysts can reduce the density, viscosity, melting point, and flashpoint. At the same time, compared to the chlorinated plastic waste, the flash point and the melting point were lower for heavy oil obtained by the pyrolysis of waste plastic containing paper.

Products obtained from batch reactor had worst transportation and storage properties than that of obtained in the tubular reactor. In general the catalysts had a positive effect on the long-term properties of light oils, however higher viscosity and lower density were found in the case of polyolefin containing paper derived light oil, than that of using chlorinated raw material by both with and without catalysts. High alkali content catalysts showed better properties for the elimination of the disadvantageous property of the hydrocarbons containing oxygen (e.g. less TAN).

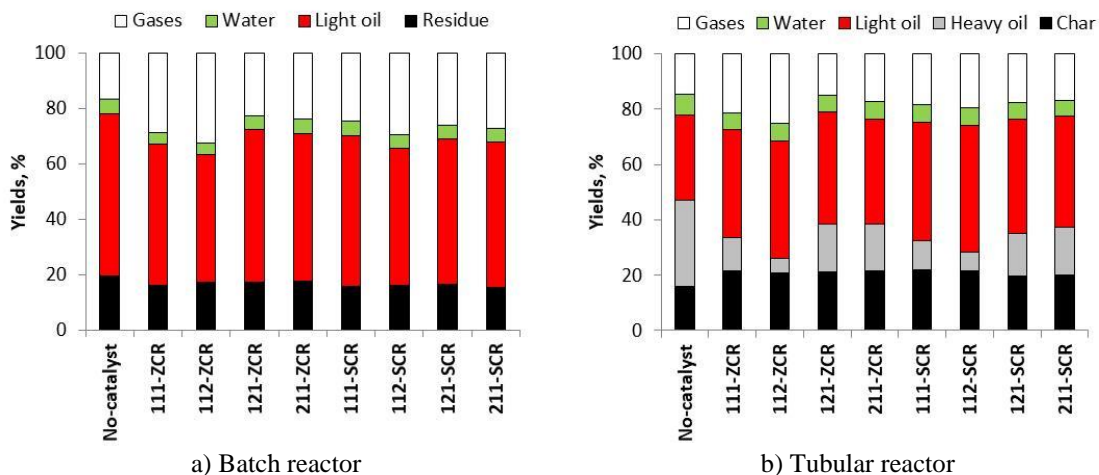
### **3.5. Pyrolysis of biomass and plastic**

In this chapter, the pyrolysis of waste plastic containing biomass and the longer-term utilization of pyrolysis oils are investigated.

#### **3.5.1. Product yields**

The yields of products obtained by batch and tubular reactor are summarized in *Figure 3.30*. Due to the cellulose in the raw material, the products contained water in addition to hydrocarbons (gases, light oil and residue). On the other hand, the amount of water was nearly half that obtained by the pyrolysis of plastic waste containing paper. The water content of the products was 4.1% in the case of the batch reactor and 5.5% when using a tubular reactor. In both cases, the amount of water was higher by 0.5-4.2% via using catalysts than that of without catalysts. Under the same conditions, more water was pro-

duced using a tubular reactor than the batch reactor. Contrary to those presented in *Section 3.3*, the water content of the products was slightly higher for both reactor designs using Ni/SAPO-11 based catalyst mixtures [293].

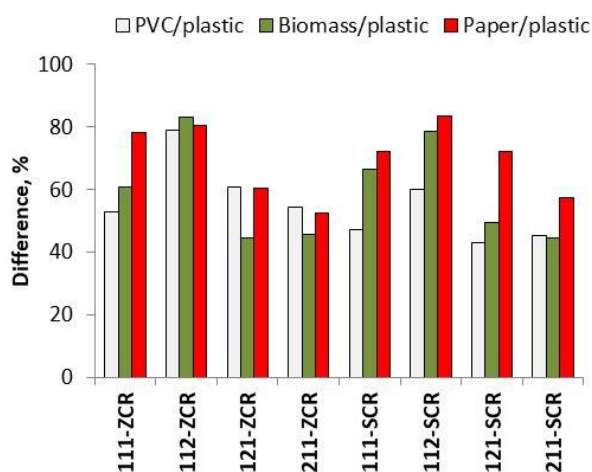


**Figure 3.30**  
The yields of pyrolysis products

The yield of gases can significantly be increased by the investigated catalysts, independently from the reactors. The yield of gases was 16.4% and 14.8% in the case of batch and tubular reactor, respectively; which is significantly less, than that of in case of plastic/paper raw material. Similarly, with the before mentioned result, any of the catalysts can significantly increase the yield of gases. It was in the range of 22.6-32.2% (batch reactor) and 15.2-25.3% (tubular reactor). However, it is worth mentioning that using both reactors, higher gas yields can be obtained by the Ni/ZSM-5 based catalyst mixtures than the Ni/SAPO-11 based catalysts. A similar result was observed in *Chapter 3.3*. Another similarity with the previous result is that the high synthetic zeolite-containing catalyst mixtures gave the highest gas yields: 112-ZCR and 112-SCR. However, the use of tubular reactor resulted in only minimal differences between the catalysts, in which case the difference between the lowest and highest gas yields was 2.7% (Ni/SAPO-11 based catalyst mixtures) and 3.4% (Ni/ZSM-5 based catalyst mixtures). For batch reactors, this value was 5.5% (Ni/SAPO-11 based catalyst mixtures) and 8.9% (Ni/ZSM-5 based catalyst mixtures) [293].

It is also well shown, that the changes in the light oil yield were similar as described in the previous chapters (*Chapters 3.2 and 3.3*). That is, in the case of batch pyrolysis, mainly due to the reactor characteristic, the amount of light oil was reduced by the use of

catalysts, while the amount of gas products increased due to the more significant decomposition. In contrast, in case of the tubular reactor, the catalysts increased not only the amount of gas products and water, but also the light oil. However, the amount of heavy oil taken as the bottom product of the distillation column decreased. The data also show that Ni/ZSM-5 based catalyst mixtures generally exhibited higher C-C cracking activity than Ni/SAPO-11 based catalysts. In both catalysts, regardless of the reactor design, the highest C-C bond breakdown can be obtained by high synthetic zeolite-containing catalyst mixtures (112-ZCR and 112-SCR). Another difference between feedstock containing PVC and paper is that when plastic containing biomass wastes had been pyrolyzed in the tubular reactor, less light oil was produced than using a PVC-plastic feedstock. The latter was mainly due to the lower water content. The difference between heavy oil and char is also striking. Comparing the three raw materials, the amount of char decreased in the order of wastes contains paper, biomass and PVC. The reason for this should be the differences in the chemical structure of the raw materials. Partly as a result, the amount of heavy oil changed in reverse order. To investigate the effect of the catalysts, it can also be seen that they had the greatest effect on the heavy oil in the case of plastic waste containing paper, that is, in these cases, the greatest difference was obtained between the catalyst-free thermal and the thermo-catalytic pyrolysis (**Figure 3.31**). This is explained by the larger C-C bond cracking resulting in more gas and liquid products.



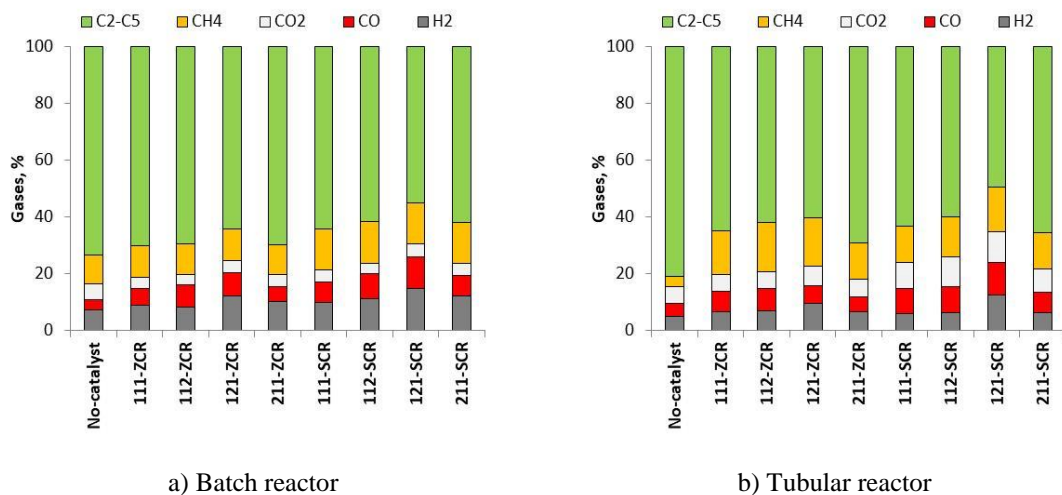
**Figure 3.31**

The difference between the heavy oil yield in case of catalyst-free and thermo-catalytic pyrolysis

### 3.5.2. Products properties

#### 3.5.2.1. Gases

The composition of gases obtained from the batch and tubular process is summarized in **Figure 3.32**. In case of batch pyrolysis, without catalyst, the gases contained 7.2 %; 3.8 %; 5.6 %; 9.9 % and 73.5 % hydrogen, CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>-C<sub>5</sub> hydrocarbons, respectively. The composition of the gas products showed great similarity in the results of experiments in batch reactor because it contained 5.1% hydrogen, 4.4% carbon monoxide, 5.9% carbon dioxide, 3.7% methane and 80.9% C<sub>2</sub>-C<sub>5</sub> hydrocarbons. As it is seen, the predominant product was the C<sub>2</sub>-C<sub>5</sub> in both cases. Comparing the result with that of obtained by the pyrolysis of waste plastic containing paper, it is clear, that less C<sub>2</sub>-C<sub>5</sub> hydrocarbon and more hydrogen, CO, CO<sub>2</sub> and CH<sub>4</sub> were found in gases in that case independently from the reactor configuration [293].



**Figure 3.32**  
The composition of gases

Catalysts can significantly decrease C<sub>2</sub>-C<sub>5</sub> concentration. It was in the range of 64.2 % -70.1 % in the case of Ni/ZSM-5 based catalyst mixture, however, using between 55.1 % and 64.3 % in the case of Ni/SAPO-11 based catalysts using batch reactor. Regarding the tubular reactor, 60.4-69.0% and 49.5-65.5% C<sub>2</sub>-C<sub>5</sub> hydrocarbons were found in the presence of Ni/ZSM-5 and Ni/SAPO-11 based catalyst mixtures, respectively.

It worth mentioning, that the increase in the ratio of red mud in the catalyst can significantly decrease the yield of C<sub>2</sub>-C<sub>5</sub> (121-ZCR and 121-SCR). However, it is also important observation, that the yield of methane was higher by using of Ni/SAPO-11 based catalysts mixture comparing to Ni/ZSM-5 based catalysts using the batch reactor, while



opposite tendency was found using the tubular reactor because the Ni/ZSM-5 based catalysts resulted in a bit higher methane yield [293].

From another point of view, there is no significant effect on the yield of carbon dioxide during the catalytic pyrolysis, for instance, it was in the range of 3.8 %-4.2 % and 3.5 % to 4.4 % by using Ni/ZSM-5 and Ni/SAPO-11 based catalyst mixture in case of a batch reactor, respectively. Regarding the tubular reactor a little bit higher CO<sub>2</sub> yields were observed in case of Ni/ZSM-5 based catalyst mixtures, and nearly double using SAPO-11 based catalysts [293].

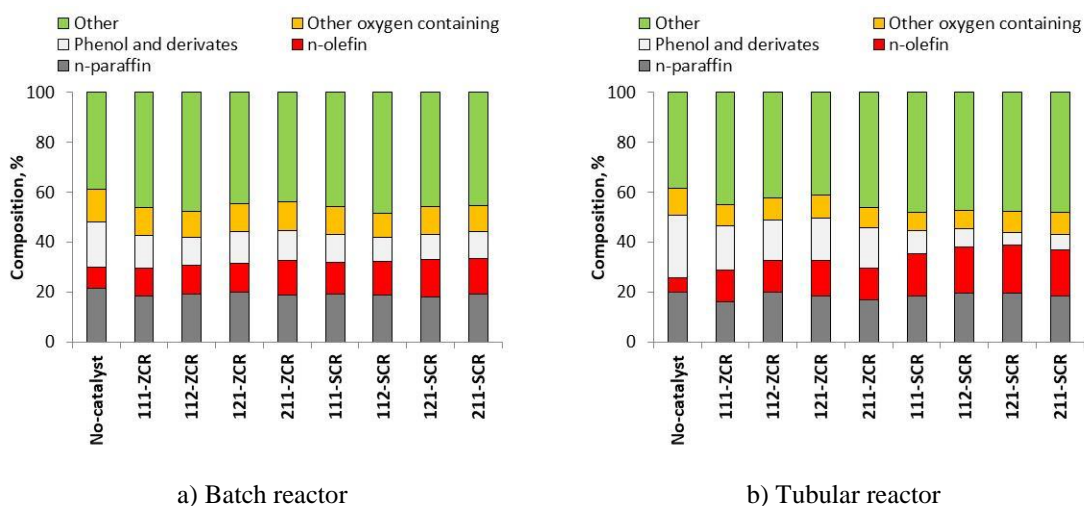
The yield of carbon monoxide has slightly increased by increasing the ratio of red mud in the catalyst; it was 8.2 % and 11.4 % (batch reactor) or 8.2% and 11.2% (tubular reactor) by the use of 121-ZCR and 121-SCR catalysts, respectively. The yield of CO was higher with 1-2% in case of the tubular reactor than that of the batch reactor. Furthermore, the yield of hydrogen has increased by the catalyst. It was in the range of 8.8 % and 12.2 % (Ni/ZSM-5 based catalyst mixture), and 9.9 %-14.7 % (Ni/SAPO-11 based catalysts mixture) in case of the batch reactor, or 6.5-9.5% (Ni/ZSM-5 based catalyst mixture), and 5.9 %- 12.4 % (Ni/SAPO-11 based catalysts mixture) in case of tubular process. The hydrogen content of the gas products was 7.2 % (batch process) and 5.2% (tubular process) without catalysts. Results also correspond to higher hydrogen yield in batch reactor and to the synergistic effect of Ni and transition metals in red mud for hydrogen production [293].

#### **3.5.2.2. Light oil**

The composition of pyrolysis oil fractions is summarized in **Figure 3.33**. According to results, the light oil contained different hydrocarbon: n-paraffin; n-olefin; phenol and its derivate (e.g. m-cresol; 2-ethyl phenol; 2,4-di methyl phenol); other oxygen-containing (aldehydes; ketones; carboxylic acid). Comparing the results from the two reactors, it can be seen that the light oils from the batch reactor had higher oxygenated content, while the concentration of phenol and derivatives was lower than that of in light oils from the tubular reactor. Catalysts had a significant effect on the concentration of different compounds. E.g., the yield of oxygenated compounds could be decreased from 13.2 % (catalyst-free case) to the range of 10.5 %-11.4 % by using of Ni/ZSM-5 based catalyst mixture, and to the range of 9.6 %-11.4 % with Ni/SAPO-11 based catalyst mixtures in case of the batch reactor [293].

Comparing the results obtained from the two reactors, it is well shown that the use of Ni/SAPO-11 based catalysts, a significant decrease was observed for the tubular reactor, whereas only a slight decrease was observed for the batch reactor. Similar results were obtained for phenol and their derivatives as their content decreased from 18.3% (catalyst-free case) to 11.0%-13.3% (Ni/ZSM-5 based catalyst) and to 9.5%-11.0% (Ni/SAPO-11 based catalyst) in a case of the batch reactor. However, there was a much more pronounced decrease in the tubular reactor, from 24.7% (no-catalyst) to 15.9-17.8% (Ni/ZSM-5 based catalysts) and 5.3-9.2% (Ni/SAPO-11 based catalysts) [289].

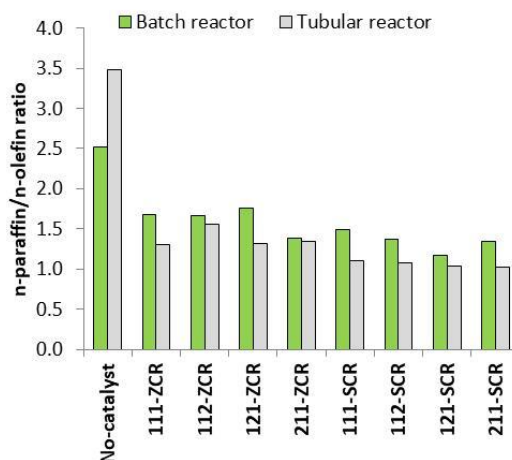
On the other hand, the yield of n-olefins has increased, while less n-paraffin can be measured by the use of catalysts. Catalysts mostly can increase the amount of other hydrocarbons, which contained especially branched molecules in case of batch pyrolysis. That result corresponded to the isomerization effect of the catalyst supporters, which was more significant in the case of the tubular reactor, especially using Ni/SAPO-11 based catalysts. It is an interesting result that n-olefins showed a significant increase, especially with Ni/SAPO-11 catalysts. However, the n-paraffin/n-olefin ratio did not differ significantly in the presence of the catalyst, although generally lower values were found for Ni/SAPO-11 based catalyst mixtures.



**Figure 3.33**  
The composition of pyrolysis oils

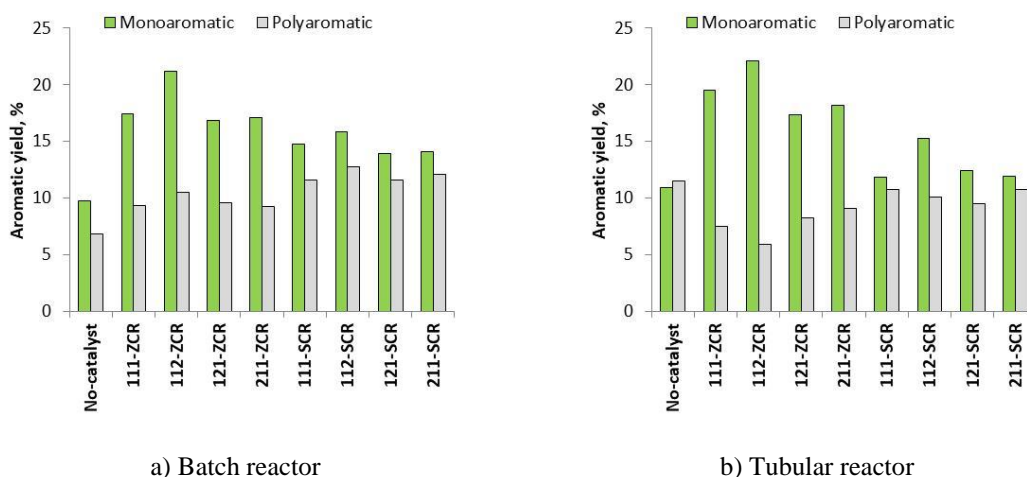
Without the catalyst, both reactors had significantly higher values: 2.5 (batch reactor) and 3.5 (tubular reactor). The catalysts clearly reduced the n-paraffin/n-olefin ratio. It is also worth mentioning that the opposite effect was observed in the presence of catalysts

than absence since the former had a higher n-paraffin/n-olefin ratio in the light oils from the batch reactor (*Figure 3.34*).



**Figure 3.34**  
The n-paraffin/n-olefin ratio of pyrolysis oils

The result of HPLC analysis is summarized in *Figure 3.35*. Results well show that the used catalysts can drastically affect both the yield of mono-aromatic and poly-aromatic hydrocarbons. The yield of mono-aromatic hydrocarbons and poly-aromatics was 9.7% and 6.8% without catalysts, which can nearly double by Ni/ZSM-5 type catalyst mixtures (16.8-21.2 %) in case of the batch reactor. The Ni/SAPO-11 catalyst mixtures has a less significant effect (13.9-15.8 %) [293].



**Figure 3.35**  
The aromatic content of pyrolysis oils and light oils

It is an important observation that opposite trend was found regarding the poly-aromatics because SAPO-11 based catalyst mixtures can increase the concentration of poly-

aromatics hydrocarbons more significantly: to 9.2-10.5% and to 11.6-12.7 % by using Ni/ZSM-5 and Ni/SAPO-11 based catalysts mixture, respectively. It is also an important difference between the two reactors that in thermo-catalytic cases the amount of polyaromatic hydrocarbons can be reduced in the case of the tubular reactor, compared to the thermal case. In parallel, the amount of mono-aromatics using Ni/ZSM-5 based catalysts can be increased significantly. This is primarily due to the higher degree of polyaromatics cracking into monoaromatic hydrocarbon. It is also clear, that the 112-ZCR catalyst had the greatest effect on the transformation of polyaromatic to monoaromatics [293].

The main properties of the light oils are summarized in **Table 3.8**. The density and viscosity changed in the range of 0.709-0.825 g/cm<sup>3</sup> and 1.918-2.735mm<sup>2</sup>/s respectively. The flash point was below 50°C.

**Table 3.8**  
Main properties of light oils obtained by pyrolysis of chlorinated waste plastics

		No-cat- alyst	111- ZCR	112- ZCR	121- ZCR	211- ZCR	111- SCR	112- SCR	121- SCR	211- SCR
Batch reactor	Colour	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown
	Density, g/cm <sup>3</sup> (at 20°C)	0.825	0.781	0.742	0.755	0.761	0.771	0.759	0.771	0.779
	Viscosity, mm <sup>2</sup> /s (at 20°C)	2.735	2.221	1.993	2.292	2.305	2.535	2.125	2.439	2.572
	Flash point, °C	<50	<50	<50	<50	<50	<50	<50	<50	<50
	TAN, mgKOH/g	9.5	8.2	7.9	5.1	4.5	7.6	6.6	3.8	4.6
Tubular reactor	Colour	Yellowish	Yellowish	Yellowish	Yellowish	Yellowish	Yellowish	Yellowish	Yellowish	Yellowish
	Density, g/cm <sup>3</sup> (at 20°C)	0.808	0.751	0.709	0.727	0.738	0.748	0.717	0.732	0.733
	Viscosity, mm <sup>2</sup> /s (at 20°C)	2.625	2.176	1.918	2.212	2.188	2.289	1.934	2.382	2.317
	Flash point, °C	<50	<50	<50	<50	<50	<50	<50	<50	<50
	TAN, mgKOH/g	7.9	4.4	4.2	3.9	3.8	5.8	5.5	5.2	5.3

### 3.5.2.3. Heavy oil

The main characteristics of the heavy oil obtained by pyrolysis of waste plastic containing biomass in a horizontal tubular reactor are summarized in **Table 3.9**. As it was mentioned previously (*subchapter 3.3.2.3*), the heavy oils have black colour and they were grease-like. According to the data in the table, the properties of heavy oils are similar to those of products obtained by the pyrolysis of other two raw materials (chlorine-containing plastic waste and biomass-containing plastic waste) in horizontal tubular reactor. In this case, the initial boiling point, the density, the viscosity, the melting point, the flash

point and the initial boiling point can be also reduced by the using of catalysts. This was due to the cracking and isomerization properties of the catalysts.

**Table 3.9**  
Main properties of heavy oils obtained by pyrolysis of waste plastics containing biomass

	No-catalyst	111-Z	112-Z	121-Z	211-Z	111-S	112-S	121-S	211-S
<b>Density, g/cm<sup>3</sup> (at 100°C)</b>	0.848	0.809	0.801	0.815	0.822	0.812	0.803	0.815	0.808
<b>Viscosity, mm<sup>2</sup>/s (at 100°C)</b>	6.12	5.06	4.52	4.79	4.54	5.03	4.09	4.43	4.17
<b>Melting point, °C</b>	85	81	80	81	82	80	78	80	82
<b>Flash point, °C</b>	216	206	198	204	208	203	201	205	203
<b>IBP, °C</b>	151	147	142	145	147	143	141	144	143
<b>FBP, °C</b>	>350	>350	>350	>350	>350	>350	>350	>350	>350
<b>Caloric value, MJ/kg</b>	40.9	41.0	41.3	40.8	41.1	41.2	40.7	41.0	40.8

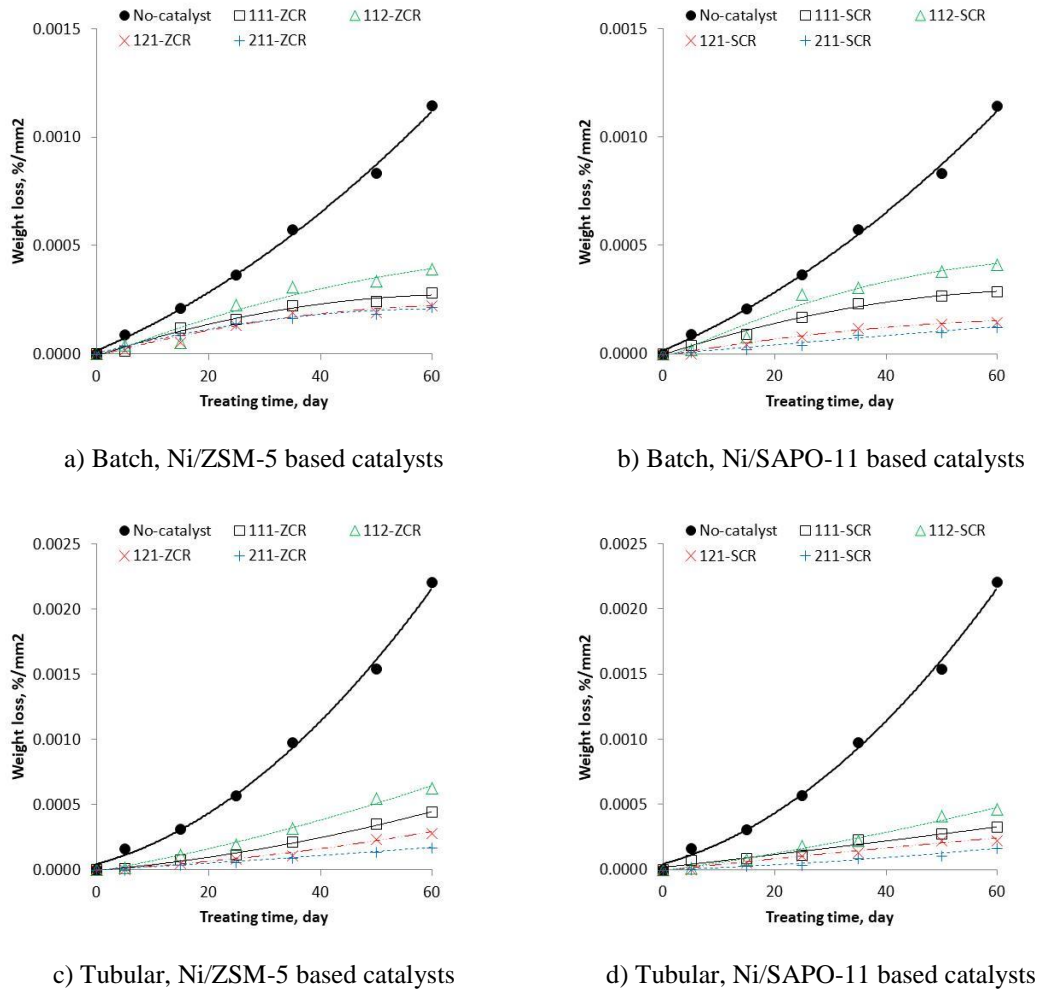
Comparing the effect of the two catalysts, it can also be said that SAPO-11 based catalyst mixtures had higher densities, lower viscosities and flash points than ZSM-5 based catalyst mixtures. It is also clear that, as before, due to the more intensive cracking of C-C bond, the 112-ZCR and 112-SCR catalysts resulted in the lowest values of density, viscosity, melting point and flash point. Regarding the calorific values, no any trend-like and significant differences between the effects of the individual catalysts can be found.

### 3.5.3. Longer-term properties of pyrolysis oils

#### 3.5.3.1. Corrosion test

The result of the corrosion test is summarized in *Figure 3.36*. Monoton increasing in the copper plate weight loss was found as a function of treating time. E.g. the weight loss of the sample plate changed from 0 → 0.0011 % and 0 → 0.0022% using batch and continuous reactor without a catalyst. Comparing the raw materials, it is clear, that a similar tendency was found in the case of waste plastic containing paper and biomass, especially using a batch reactor. The degree of weight loss was exponential in both cases without catalysts. The weight loss changed almost linearly using raw material containing PVC in case of the batch process. However, significant differences were observed between the effects of the raw materials in the products obtained by the continuous reactor. In this case, the relationship was logarithmic using waste polymer/PVC raw material, linear for polymer/paper waste and exponential for polymer/biomass waste regarding the corrosion test of pyrolysis oils obtained without the catalyst. Comparing raw materials

containing biomass and paper wastes, a similar amount of weight loss was found, although less weight loss was demonstrated in case of the batch process using plastic and biomass raw material, or in the case of the tubular reactor using waste plastic and paper raw material.



**Figure 3.36**  
Weight loss of the copper plate sample during the corrosion test

Catalysts had an advantageous effect on the corrosion properties of the pyrolysis oils because they can significantly be decreased weight loss. On one hand, there was not a significant difference between the Ni/ZSM-5 and Ni/SAPO-11 based catalyst mixtures using a batch reactor. On the other hand, Ni/SAPO-11 based catalyst mixtures can decrease the weight loss to a greater extent using a tubular reactor. It is also well shown, that the catalyst efficiency was independent of the reactor configuration because it follows the order of 112-ZCR, 111-ZCR, 121-ZCR and 211-ZCR in case of Ni/ZSM-5 based catalyst mixtures and 112-SCR, 111-SCR, 121-SCR and 211-SCR using Ni/SAPO-11

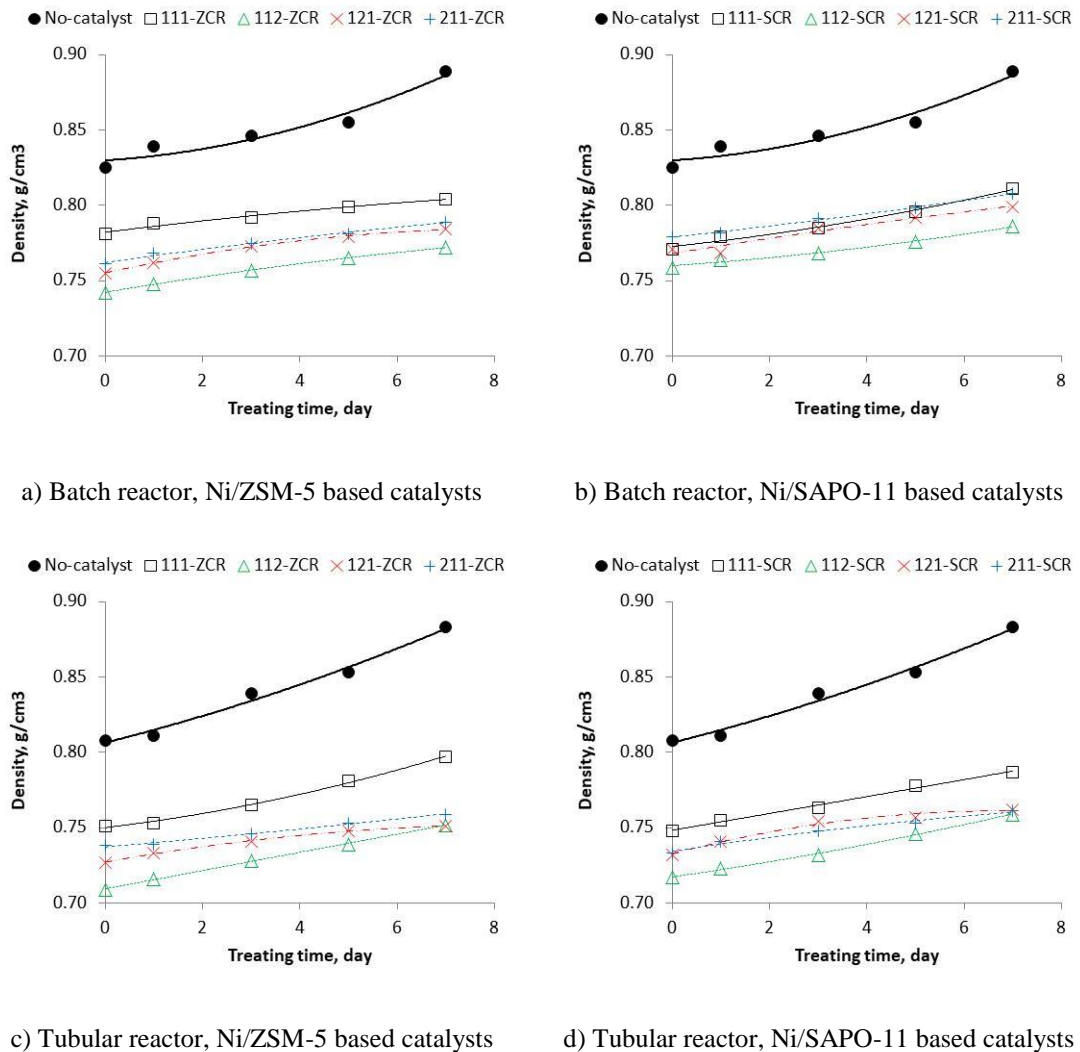
based catalyst mixtures. The change in a weight loss of the copper test sheet was logarithmic for the batch reactor system and exponential for the continuous reactor using catalysts, although the rate of increase was significantly below that of the corrosion test for pyrolysis oil without the catalyst.

The degree of the positive effect of catalysts on pyrolysis oil corrosion properties was mostly similar to that obtained with waste plastic/PVC mixtures. In that case, it was found that the weight loss of the test copper plate at day 60<sup>th</sup> in the thermo-catalytic case was one-third of the weight loss obtained in the catalyst-free case. Comparing the before mentioned result with the weight loss in case of waste plastic/biomass sourced pyrolysis oil, it is clear, that it was 19-34% (Ni/ZSM-5 based catalyst mixtures) and 11-36% (Ni/SAPO-11 based catalyst mixtures) of the weight loss in case of catalyst-free pyrolysis using batch reactor. The same property was 8-28% (Ni/ZSM-5 based catalyst mixtures) and 8-21% (Ni/SAPO-11 based catalyst mixtures) of the result obtained without the catalyst for the tubular reactor. In each case, the high red mud and Ca(OH)<sub>2</sub> content of catalysts resulted in less change in weight. By way of comparison, it is worth mentioning that the use of catalysts had a much smaller positive effect in the case of waste plastic/paper waste. Therefore, the positive effect of the catalysts was independent of the cellulose presence in the raw materials (both biomass and paper consisting of cellulose units) rather it was due to the chemical structure of compounds obtained from the decomposition reactions.

### ***3.5.3.2. Accelerated aging test***

The results of accelerated aging tests are summarized in **Figures 3.37-3.40**. **Figure 3.37** illustrates the change in the density of pyrolysis oils over time for different reactor types. The graphs well show that the density of the samples increased monotonically over the length of the study. This is similar to the aging characteristics of the pyrolysis products from the other two raw materials. However, the reactor configuration used and the presence or composition of the catalysts significantly influenced the results obtained. In the case of batch pyrolysis without the catalyst, higher values than the linear correlation was observed, while a nearly linear relationship was found as a function of time in case of the tubular reactor. On the 7<sup>th</sup> day, the rate of increase was 7.7% for the batch reactor and 9.2% for the continuous reactor. In both cases, the used catalysts can significantly reduce the rate of density increase. During batch pyrolysis, the density increase varied between 2.94-4.0% (Ni/ZSM-5 based catalysts) and 3.6-5.2% (Ni/SAPO-11 based catalysts),

while the same increase was found with 2.8-6.1% (Ni/ZSM-5 based catalysts) and 3.8-5.9% (Ni/SAPO-11 based catalysts) regarding products from tubular reactor. On the other hand, there were no significant differences either in the structure of zeolites or in the equipment to be used. It is important to mention, however, that in each case the catalysts with large synthetic zeolite content produced the highest growth (112-ZCR and 112-SCR). At the same time, due to the cracking characteristic of the synthetic zeolites, these products had the lowest initial density.



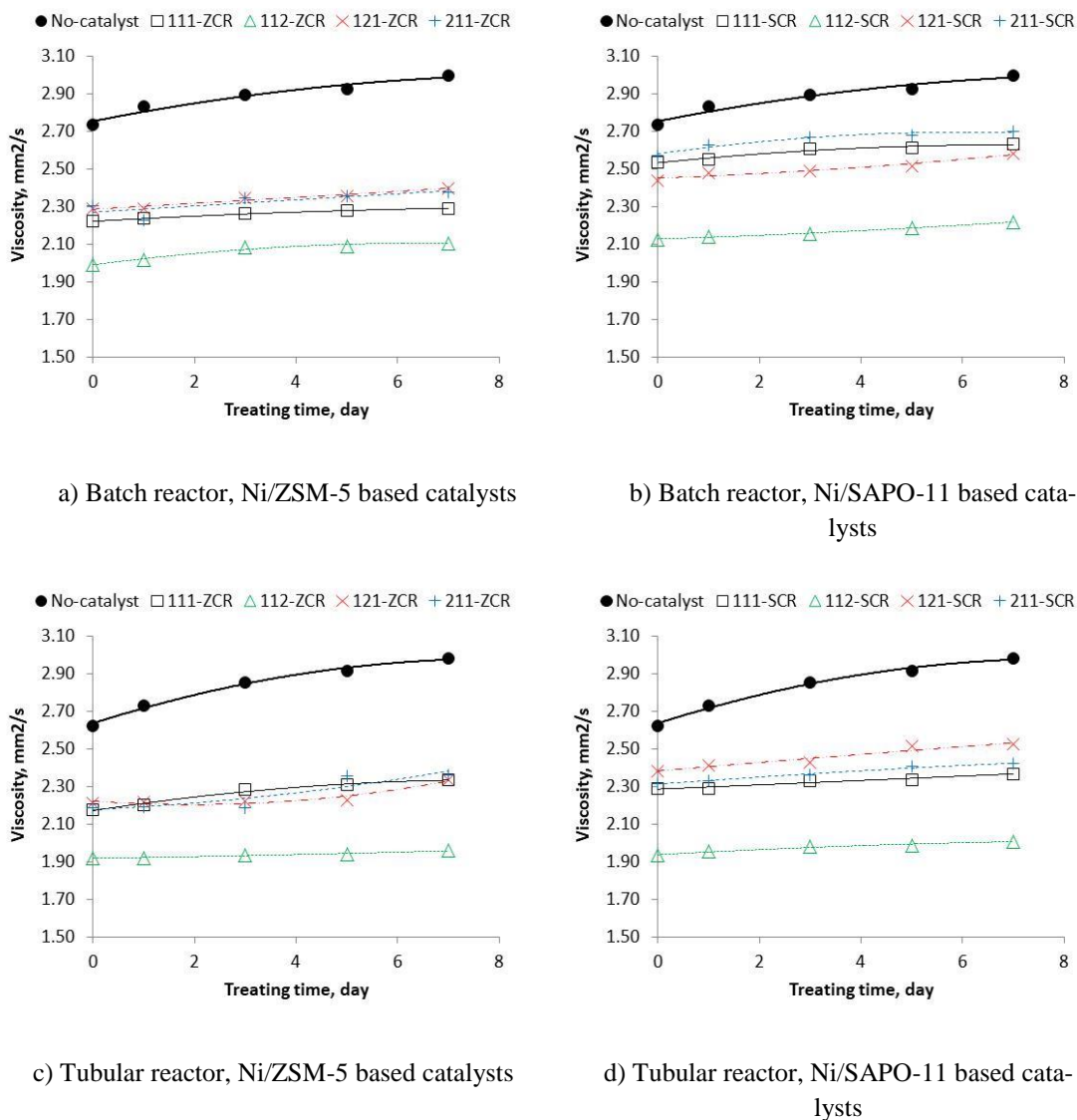
**Figure 3.37**  
The density of pyrolysis oils during the aging test

Comparing the investigated raw materials, it can be seen that in the case of waste plastics/paper mixtures resulted in lower density values in case of both batch pyrolysis and tubular reactor. Furthermore, the degree of density increase for the waste plastic/biomass feedstock was lower than the results for waste plastic/paper feedstock using both



batch reactor and continuous reactor. It was independent of the presence and composition of the catalysts.

The viscosity values obtained from accelerated aging tests are shown in **Figure 3.38**. As discussed in the previous chapters, density and viscosity showed a correlation.



**Figure 3.38**  
The viscosity of pyrolysis oils during the aging test

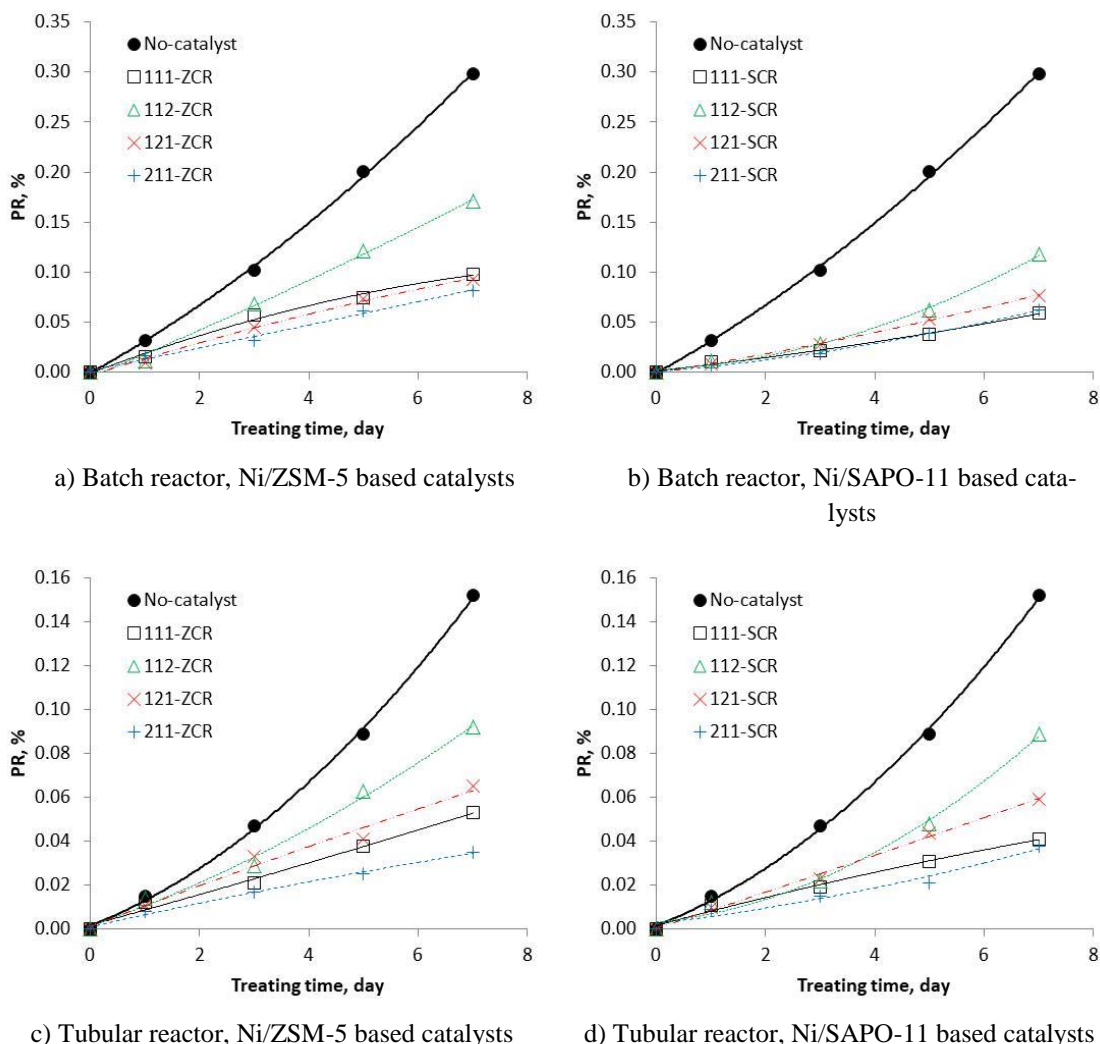
The viscosity of the non-catalytic product of batch pyrolysis increased from 2.735mm<sup>2</sup>/s to 2.998mm<sup>2</sup>/s (9.6% increase), while it changed from 2.625mm<sup>2</sup>/s to 2.982mm<sup>2</sup>/s (13.6% increase) in case of the tubular reactor. The initial viscosity values for both reactors were higher than those for waste plastic/paper feedstock or waste plastic/PVC feedstock. However, in a batch reactor, the viscosity of the pyrolysis oils pro-

duced without catalysts can increase in the order of the waste plastics/PVC < waste plastics/biomass < waste plastics/paper raw materials, while in the case of a continuous reactor the order was waste plastics/paper < waste plastics/biomass < waste plastics/PVC raw materials.

The catalysts resulted in a significantly lower viscosity than density. The change (decreasing) of the viscosity of the liquid product was 48-66% regarding batch reactor and 56-85% in the case of a continuous reactor compared to the catalyst-free experiments. The catalytic effect was more significant than that of the other two feedstocks. To compare the viscosity and density values, it is important to mention, that the high synthetic zeolite-containing catalyst mixtures also exhibited the highest decrease in viscosity change (112-ZCR and 112-SCR), although they had the lowest initial values. This result is different from that obtained by the use of waste plastics/PVC or waste plastics/paper raw materials, in which case the 112-ZCR and 112-SCR catalysts resulted in the lowest viscosity increase.

*Figure 3.39* summarizes the amount of material deposited during accelerated aging tests that indicate storage characteristics. Similarly to the other two raw materials, in this case, there was an increasing tendency for the amount of material deposited on the filter. In the absence of catalysts, 0.298% (batch reactor) and 0.152% (continuous reactor) polymerous materials were precipitated, which could be reduced by the use of catalysts. Compared to the other two raw materials, this set had the least amount of precipitated material. The amount of material deposited decreased in the order of the waste plastic/paper > waste plastic/biomass > waste plastic/PVC feedstock, which was independent of the reactor configuration. However, without the use of a catalyst, the rate of growth was quicker for the pyrolysis oils obtained from the tubular reactor than from the batch reactor. Comparing the raw materials it can be seen that the growth tendency was similar for the waste plastic/PVC and waste plastic/biomass raw materials without the catalyst, while similarities for the order of the catalysts was found regarding waste plastic/biomass and waste plastic/paper raw materials containing cellulose units. 112-ZCR and 112-SCR catalysts showed the least precipitation at day 7 for the waste plastic/PVC feedstock, while that catalyst showed the least positive effect regarding the other two raw materials. This is partly due to the higher portion of the products obtained from the thermal reactions and

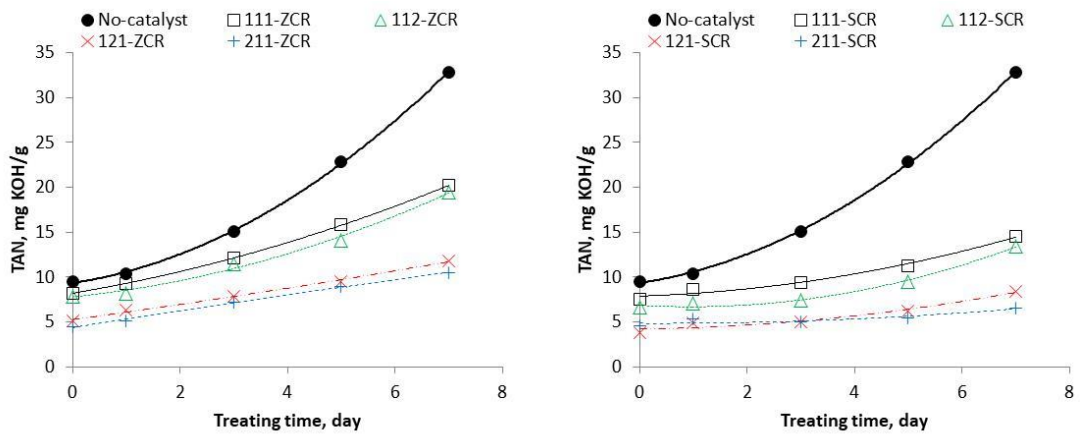
partly due to the lower cracking and isomerizing effect of the catalysts. Mainly the blocking of the active sites of the catalyst by molecule fragments from the cellulose unites or even steric reason can be blamed.



**Figure 3.39**  
Polymer-oligomer residue on the filter after the aging test

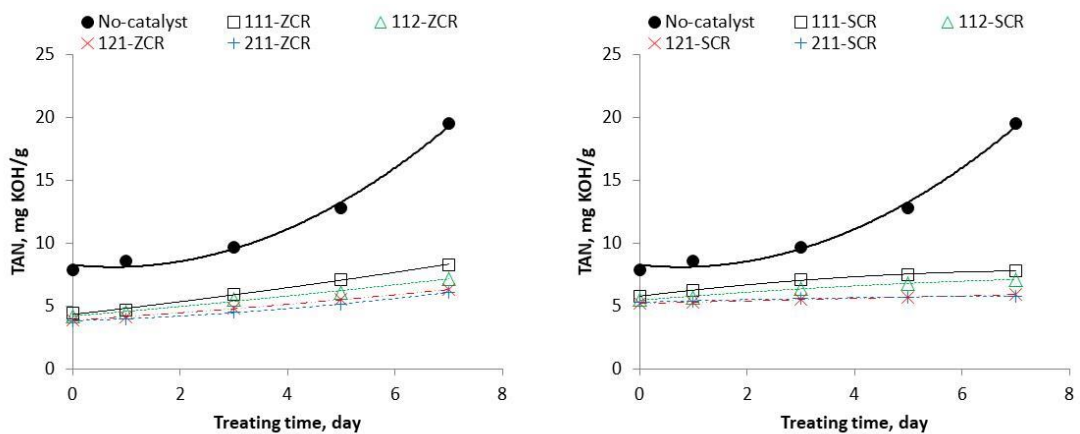
The TAN characteristics of pyrolysis oils are shown in **Figure 3.40**. The results obtained from the plastic waste/biomass feedstock are similar to the TAN results regarding the pyrolysis oils obtained from the plastic waste/paper stock using a batch reactor. In both cases, the increase in TAN was exponential, primarily in the absence of the catalyst. When the tubular reactor was used, the change of pyrolysis oil TAN was linear for the plastic waste/paper feedstock, while it was also exponential for the plastic waste/biomass feedstock. However, there is a significant difference in TAN values, which decreased in

the order of plastic waste/paper > plastic waste/biomass > plastic waste/PVC, independently from the reactors to be used. Comparing the two feedstocks containing cellulose, there was a significant difference regarding the results from the batch reactor because the TAN of the pyrolysis oil obtained from plastic waste/paper (19.7 mgKOH/g → 62.7mg KOH/g) was nearly twice that of in case of plastic waste/biomass feedstock (9.5 mgKOH/g → 32.8mg KOH/g). In the case of the tubular reactor, no significant difference was found; 15.2 mgKOH/g → 22.3mg KOH/g (plastic waste/paper) and 7.9 mgKOH/g → 19.5mg KOH/g (plastic waste/biomass). At the same time, the rate of increase was the highest for the pyrolysis oil obtained from the plastic waste/biomass feedstock, independently from the reactor design. Another significant difference is that in the batch reactor, the 111-ZCR, 112-ZCR, 111-SCR and 112-SCR catalysts can not reduce the rate of TAN increase compared to the non-catalyst pyrolysis.



a) Batch reactor, Ni/ZSM-5 based catalysts

b) Batch reactor, Ni/SAPO-11 based catalysts



c) Tubular reactor, Ni/ZSM-5 based catalysts

d) Tubular reactor, Ni/SAPO-11 based catalysts

**Figure 3.40**  
Total Acid Number of the liquid fractions after the aging test

In contrast, pyrolysis oil obtained from plastic waste/biomass feedstock had a lower TAN growth rate in the thermo-catalytic cases on day 7 than in the absence of the catalyst. Alkaline catalysts (121-ZCR, 211-ZCR, 121-SCR and 211-SCR) can clearly reduce the TAN for pyrolysis oil from batch reactors. Those curves were well distinguished from results using 111-ZCR, 112-ZCR, 111-SCR and 112-SCR catalysts. However, there was no such difference among the pyrolysis oil TAN values obtained by the thermo-catalytic pyrolysis of waste polymer/biomass from the continuous reactor.

#### **3.5.4. Main conclusions of biomass and plastic pyrolysis**

Products contained water in addition to hydrocarbons, while the water yield was approximately 50 % lower than that obtained by the pyrolysis of plastic waste containing paper. Catalysts can expressively increased the yield of gases. Comparing the three raw materials, the amount of char decreased in the order of wastes contains paper, biomass, and PVC. However, the amount of heavy oil changed in reverse order. In terms of gas composition, catalyst has no significant effect to yield of carbon dioxide. The yield of oxygenated compounds in light oils could be decreased by catalysts, while light oils from the batch reactor had more oxygenated compounds. Due to the aromatization effect of the catalyst, the yield of mono-aromatic and poly-aromatic hydrocarbons can be drastically increased. The ZSM-5 based catalyst increases the yield of mono-aromatic, while SAPO-11 based catalyst mixtures can increase the concentration of poly-aromatics hydrocarbons. The properties of heavy oils were similar to those obtained by the pyrolysis of the other two raw materials (chlorine-containing plastic waste and paper-containing plastic waste) in a horizontal tubular reactor.

Regarding the aging and corrosion tests, the copper weight loss follows exponential for polymer containing biomass raw material without catalyst. Catalysts can significantly reduce the corrosion rate and no significant difference was between the two zeolites using batch reactor, while the Ni/SAPO-11 based catalyst mixtures can decrease the weight loss to a greater extent using a tubular reactor. The rate of density, viscosity, polymer-oligomer residue and TAN increase can be significantly reduced by catalysts. The degree of density increase was independent from the presence and composition of the catalysts. The rate of growth was quicker for the pyrolysis oils obtained from the tubular reactor than from the batch reactor without the use of a catalyst. Alkaline catalysts can clearly reduce the TAN for pyrolysis oil, especially using batch reactor.

## 4. CONCLUSION

In this chapter the main results of the real waste pyrolysis and the stability of the light oils are concluded. **Table 4.1** summarizes the main effect of the different reaction parameters regarding the properties.

**Table 4.1**  
The effect of different parameters on properties

Property	Aim	Chlorinated plastic waste		Plastic waste containing paper		Plastic waste containing biomass	
		Batch	Tubular	Batch	Tubular	Batch	Tubular
Gas yield (%)	Max.	26.2 112-ZCR	28.7 112-ZCR	38.2 112-ZCR	27.5 112-ZCR	32.2 112-ZCR	25.3 112-ZCR
Light oil yield (%)	Max.	79.6 Thermal	53.7 112-SCR	33.1 Thermal	32.1 112-SCR	58.6 Thermal	45.8 112-SCR
Water (%)	Min.	N/A	N/A	10.7 112-ZCR	8.9 112-SCR	4.3 12-ZCR	5.7 211-SCR
Hydrogen in gas (%)	Max.	6.1 121-SCR	5.4 121-SCR	17.3 211-SCR	15.7 121-SCR	14.7 121-SCR	12.4 121-SCR
Chlorine in gas (ppm)	Max.	57000 211-SCR	47000 211-ZCR	N/A	N/A	N/A	N/A
Chlorine in light oil (ppm)	Min.	228 211-SCR	327 211-SCR	N/A	N/A	N/A	N/A
n-olefin/n-paraffin in light oil	Min.	0.7 112-SCR	1.1 Thermal	0.58 111-SCR	0.77 121-SCR	0.4 Thermal	0.3 Thermal
Phenol and derivatives in light oil (%)	Min.	N/A	N/A	8.5 112-ZCR	6.2 121-SCR	9.5 112-SCR	5.3 121-SCR
Other oxygenated in light oil (%)	Min.	N/A	N/A	15.0 121-ZCR	12.8 111-SCR	9.6 112-SCR	7.1 112-SCR
Monoaromatic in light oil (%)	Max.	5.7% 211-ZCR	4.1% 121-SCR	22.1 112-SCR	22.9 112-ZCR	21.2 112-ZCR	22.1 112-ZCR
Polyaromatic in light oil (%)	Min.	- Thermal	- Thermal	9.4 112-ZCR	5.8 112-ZCR	6.8 Thermal	5.9 112-ZCR
Aging test							
Weight loss, %/mm <sup>2</sup>	Min.	0.025 211-SCR	0.0308 121-SCR	9.2*10 <sup>5</sup> 121-ZCR	8.5*10 <sup>5</sup> 211-ZCR	0.0001 211-SCR	0.0002 211-SCR
Polymeric-oligomer, %	Min.	0.05 112-ZCR	0.003 112-ZCR	0.106 211-SCR	0.079 211-SCR	0.059 111-SCR	0.035 211-ZCR
TAN change*, %	Min.	40.0 211-SCR	10.3 121-SCR	108.9 121-ZCR	8.9 121-ZCR	43.9 211-SCR	9.4 211-SCR
Density change*, %	Min.	1.75 211-SCR	0.51 211-SCR	2.33 211-SCR	2.77 121-SCR	2.95 111-ZCR	2.85 211-ZCR
Viscosity change*, %	Min.	6.33 121-ZCR	3.07 112-ZCR	7.66 121-ZCR	7.23 121-ZCR	3.19 111-ZCR	2.14 112-ZCR

Max. – maximizing, Min. - minimizing

\* Change = (min. value at 7<sup>th</sup> day – original value at 0 day)/ original value at 0 day\*100

In terms of gas yield and regardless of the used raw materials, the Ni/ZSM-5 based catalyst (112-ZCR) has shown the best results. On the other hand, the yield of light oil was at its highest level by using the Ni/SAPO-11 based catalyst (112-SCR) with the tubular reactor and by thermal pyrolysis with the batch reactor. With reference to the water yield, no significant differences were found by comparing the used catalyst and reactor.

As a result of the synergistic effect, the Ni/SAPO-11 based catalyst with a high ratio of red mud (121-SCR) has produced the highest yield of hydrogen regardless of the used raw materials or the used reactor configuration. In connection with the n-olefin/n-paraffin ratio in the light oil, the thermal and the Ni/SAPO-11 based catalyst showed the best results. The chlorinated compounds in the light oil were at their lowest value by using Ni/SAPO-11 based catalyst with a high ratio of calcium hydroxide (211-SCR) with the batch reactor. On another note, by utilizing the tubular reactor and Ni/SAPO-11 based catalyst with the high ratio of red mud (121-SCR) the lowest level of phenol and derivatives in light oil was yielded. The Ni/SAPO-11 based catalyst (112-SCR) has yielded the least yield of oxygenated compounds in light oil (aldehydes, ketones, carboxylic acids, etc.). Irrespective of the reactor configuration, the high synthetic zeolite content (112-ZCR and 112-SCR) catalysts can increase significantly the yield of monoaromatic hydrocarbons, while the thermal pyrolysis yield more polyaromatic compounds.

In the matter of light oils stability, as regards to copper plate weight loss, TAN, and density, the catalysts with high alkaline content ( $\text{Ca(OH)}_2$ , red mud) (121-ZCR, 211-ZCR, 121-SCR, 211-SCR) especially with Ni/SAPO-11 based catalyst were the most effective in reducing the TAN, density increase and weight loss of copper plate. From another point of view, it can be seen that Ni/ZSM-5 based catalyst with high alkali content (121-ZCR, 211-ZCR) has an optimum efficiency in suppressing the increasing rate of the viscosity and oligomer formation. By way of comparison between the batch and continuous reactor it becomes apparent that the tubular reactor has produced an oil with enhanced quality and stability.

## 5. SUMMARY

Since the synthesis of the first plastic in the early 1900s, and owing to their favourable properties, plastics have replaced many other materials such as ceramics, metals and, wood. The combination of the increasing plastics production and their short lifetime results in an increasing amount of waste plastics that have to be managed each year. For a long time, the plastic and biomass waste, like the rest of household waste, was mainly landfill. However, the landfill of municipal waste poses various environmental problems. Consequently, various local and European laws have advocated the reduction of the landfill of waste in favor of recycling or energy recovery.

Thermochemical processes are distinguished according to the nature of the oxidizing agent presence: combustion (excess air), pyrolysis (no oxidant) and gasification (insufficient oxidant, steam, CO<sub>2</sub>, etc.). The pyrolysis looks attractive way for transforming of polymer wastes into valuable fractions, however the long term utilization of the products needs further investigations. Especially the unfavoured compounds in the pyrolysis products can cause further serious problems (e.g. catalyst poisoning, erosion, corrosion, etc.).

The pyrolysis and co-pyrolysis of different raw materials (plastic, biomass and paper) and the long term stability of light oils as liquid product of the pyrolysis were investigated during my PhD thesis work using different catalysts and reactors. The main aims of my research work was the following:

- a) to investigate the effect of different raw materials, reactor configurations, and catalysts mixtures in terms of in-situ upgrading of pyrolysis products;
- b) improving in corrosion, transportation and storage properties of real waste-derived pyrolysis oil to obtain valuable hydrocarbons for an energetic, refinery or even petrochemical application;
- c) investigate the correlation between the accelerated and non-accelerated aging process of the pyrolysis oils.

Firstly, the tested catalysts were prepared, then the used test methods were investigated and compared. Correlation was found between the accelerated and non accelerated aging, however the significance of the correlation was fundamentally affected by the source and composition of the tested liquid hydrocarbon fraction.

Regarding the pyrolysis of chlorinated plastic waste, it was found that Ni/ZSM-5 based catalysts could increase the yields of gases and light oil. Catalysts can also increase the yield of methane, ethylene, ethane and branched hydrocarbons. Nevertheless, the high



concentration of red mud in the catalysts can increase the yield of hydrogen and the saturated *i*-C<sub>4</sub> had a lower concentration than unsaturated *i*-C<sub>4</sub>. Light oils had a range of C<sub>5</sub>-C<sub>35</sub> hydrocarbons while the presence of catalyst supported the aromatization and saturation reactions. ZSM-5 based catalysts show high efficiency in aromatization reaction. The use of catalysts with high Ca(OH)<sub>2</sub> and red mud catalysts content can decreased significantly the concentration of chlorinated mono-aromatics and exhibited beneficial long term properties such as decreasing in acidic compounds, reduction in density, and reduction in the solid deposition.

Catalysts had also beneficial property to the product yields during the pyrolysis of biomass and plastic waste under a mild condition. Catalysts has significantly increased the yield of gases as a result of its C-C bound cracking effect. On the other hand, due to the presence of biomass water was found in the products, which can reduce the quality of the obtained fraction by inducing many issues in the case of the long-term application, like corrosion and phase separation. The yield of water was not affected by different catalysts. On the other hand, the presence of catalyst has substantially reduced the yield of residue. The increase in the ratio of red mud in the catalyst has affected the gas yield composition by decreasing the yield of C<sub>2</sub>-C<sub>5</sub> hydrocarbons. However, those catalysts can promote the formation of hydrogen.

On the contrary, the yields of oxygenated compounds in light oil (aldehydes, ketones, carboxylic acids, etc.) can significantly decreased by the using of catalysts, which can improve the quality of liquid hydrocarbons by increasing its energy density and stability.

By way of comparison between the Ni/ZSM-5 and Ni/SAPO-11 catalyst mixtures, due to the larger pore areas and higher Si/Al ratio, the Ni/ZSM-5 containing catalysts mixture resulted in higher yield in gases, than Ni/SAPO-11 based catalysts. Catalysts can isomerize the main carbon frame of gases (especially using catalysts with a high concentration of Ni/ZSM-5 and Ni/SAPO-11), and promote the production of unsaturated hydrocarbons. Nonetheless, it slightly increases the ratio of *n*-olefin and *n*-paraffin.

Independently from the raw materials, high concentration of red mud led to the highest proportion of hydrogen in gas products. Furthermore, SAPO-11 based catalysts can promote the hydrogen yield. Similarly, in case of SAPO-11 containing catalyst the concentration of unsaturated branched hydrocarbons, especially isobutene, trans-but-2-en and cis-but-2-en were remarkably high.

In term of stability and long-term utilization, the density and viscosity were only slightly increased, however it was affected also by the composition of raw materials and

the presence of catalysts. By comparing to the catalyst free thermal and thermo-catalytic pyrolysis, catalysts can slow the aging process. However, the aging of pyrolysis oils obtained by Ni/SAPO-11 containing catalyst takes earlier than that of Ni/ZSM-5. Conversely, acidic components can cause more significant change in both TAN or even in the case of the corrosion test. In the case of the catalytic pyrolysis and especially SAPO-11 based catalysts, both the TAN and relative change in copper plate weight loss during the corrosion test were lower. Regarding the chlorinated compounds (in case of pyrolysis of chlorinated raw material), by the using of catalysts – especially the presence of red mud and  $\text{Ca}(\text{OH})_2$  – the chlorine could be transformed largely into gaseous products and the chlorine concentration in pyrolysis oils can further be decreased. Despite that, the Ni/SAPO-11 exhibited better properties for chlorine reduction than Ni/ZSM-5 based. On the other hand, as a result of the presence of PVC in the raw materials, organic chlorinated hydrocarbons (chloromethane and chloroethane) have been detected in the gas fraction. In term of chlorine removal, Ni/SAPO-11 based catalysts showed advanced properties in dechlorination and the significant reduction in the weight loss of copper plate in the course of the aging test. Meanwhile, the chlorine content of the solid residue increased considerably.

From another point of view, the co-pyrolysis of plastic and paper (newspaper and cardboard) waste under mild condition and by utilizing two different reactors batch and continuous have demonstrated that catalysts can increase the yield of volatiles and improve product properties such as density, viscosity and TAN. It is worth mentioning that the presence of newspaper and cardboard in the raw materials was the reason for the appearance of water and a wide range of oxygenated compounds in the liquid product. The yield of water was not considerably affected by introducing the catalyst. On the other hand, the use of different catalyst mixture had an advantageous effect on the pyrolysis products such as decreasing the yield of  $\text{CO}_2$  and oxygenated compounds and promote the yield of methane and hydrogen.

In accordance with the aging tests, it has been identified that the tubular reactor had produced an oil with a better transportation and storage stability characteristics than those oils acquired by using the batch reactor. However, future research should enhance the durability, reliability and flexibility of the new catalysts, in order to develop a new generation of pyrolysis processes, which are highly adaptable and adjustable to various product specifications. Diversification of pyrolysis feedstock types supports the adaptation of

this new technology in different regions and nation state. On the other hand, the environmental and economic impacts of pyrolysis process must be quantified in the framework of the global energy supply market.

Based on the work presented in this thesis the following recommendations for the future research can be suggested:

- a) life cycle assessment of different thermochemical waste recycling procedures,
- b) experimental investigation on pyrolysis reactor scale-up,
- c) detailed investigation of the economic profitability of the different pyrolysis processes,
- d) in-depth understanding of the influence of plastic additives and filler on the pyrolysis products' quality,
- e) deep understanding of the principal physical and chemical phenomena-taking place at the catalyst scale, since that would help to improve the design and the selection of a catalyst,
- f) selection and optimization of a pyrolysis reactor that shows high flexibility and adaptability with various feedstock materials.
- g) investigation of the co-pyrolysis behavior of mixed polymeric waste materials for pyrolysis without and with catalysts in different reactors,
- h) post-treating of pyrolysis products to obtain valuable fractions.

## References

- [1] M.H. Duku, S. Gu, E. Ben Hagan, A comprehensive review of biomass resources and biofuels potential in Ghana, *Renew. Sustain. Energy Rev.* 15 (2011) 404–415. <https://doi.org/10.1016/j.rser.2010.09.033>.
- [2] S.K. Behera, P. Srivastava, R. Tripathi, J.P. Singh, N. Singh, Evaluation of plant performance of *Jatropha curcas* L. under different agro-practices for optimizing biomass – A case study, *Biomass and Bioenergy*. 34 (2010) 30–41. <https://doi.org/10.1016/j.biombioe.2009.09.008>.
- [3] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, C. Roy, Characterization of bio-oils in chemical families, *Biomass and Bioenergy*. 31 (2007) 222–242. <https://doi.org/10.1016/j.biombioe.2006.02.006>.
- [4] F. Ardente, G. Beccali, M. Cellura, Eco-sustainable energy and environmental strategies in design for recycling: the software “ENDLESS,” *Ecol. Modell.* 163 (2003) 101–118. [https://doi.org/10.1016/S0304-3800\(02\)00418-0](https://doi.org/10.1016/S0304-3800(02)00418-0).
- [5] J.Z. Buchwald, *Energy and Empire*, *Br. J. Hist. Sci.* 24 (1991) 85–94. <https://doi.org/10.1017/S0007087400028478>.
- [6] Y. Guo, T. Yeh, W. Song, D. Xu, S. Wang, A review of bio-oil production from hydrothermal liquefaction of algae, *Renew. Sustain. Energy Rev.* 48 (2015) 776–790. <https://doi.org/10.1016/j.rser.2015.04.049>.
- [7] R. Chipman, *Natural Resources and Economic Development - By Edward B. Barbier*, *Nat. Resour. Forum.* 30 (2006) 333–334. [https://doi.org/10.1111/j.1477-8947.2006.116\\_2.x](https://doi.org/10.1111/j.1477-8947.2006.116_2.x).
- [8] J.K. Knudsen, *Renewable Energy and Environmental Policy Integration: Renewable Fuel for the European Energy Policy?*, in: *Eur. Energy Policy*, Edward Elgar Publishing, 2012: pp. 48–65. <https://doi.org/10.4337/9780857939210.00011>.
- [9] *Industrial Development Report 2018*, UN, 2018. <https://doi.org/10.18356/b0cad365-en>.
- [10] OECD iLibrary | GDP, population and consumption, (n.d.). [https://www.oecd-ilibrary.org/environment/environment-at-a-glance-2015/gdp-population-and-consumption\\_9789264235199-23-en](https://www.oecd-ilibrary.org/environment/environment-at-a-glance-2015/gdp-population-and-consumption_9789264235199-23-en) (accessed March 13, 2020).
- [11] S. Sharma, IV. THE OIL INDUSTRY AND THE ECONOMY, in: *Role Pet. Ind. Singapore’s Econ.*, ISEAS–Yusof Ishak Institute Singapore, Singapore, 1989: pp. 9–25. <https://doi.org/10.1355/9789814376297-005>.
- [12] J. Soussan, *Primary resources and energy in the third world*, Taylor and Francis, 2019. <https://doi.org/10.4324/9780429278556>.
- [13] *Key World Energy Statistics 2014*, OECD, 2014. [https://doi.org/10.1787/key\\_energ\\_stat-2014-en](https://doi.org/10.1787/key_energ_stat-2014-en).
- [14] *Key World Energy Statistics 2017*, OECD, 2017. [https://doi.org/10.1787/key\\_energ\\_stat-2017-en](https://doi.org/10.1787/key_energ_stat-2017-en).
- [15] *Key World Energy Statistics 2019*, OECD, 2019. <https://doi.org/10.1787/71b3ce84-en>.
- [16] *World Energy Outlook 2017*, OECD, 2017. <https://doi.org/10.1787/weo-2017-en>.
- [17] K. Ding, A. He, D. Zhong, L. Fan, S. Liu, Y. Wang, Y. Liu, P. Chen, H. Lei, R. Ruan, Improving hydrocarbon yield via catalytic fast co-pyrolysis of biomass and plastic over ceria and HZSM-5: An analytical pyrolyzer analysis, *Bioresour. Technol.* 268 (2018) 1–8. <https://doi.org/10.1016/j.biortech.2018.07.108>.
- [18] United nations conference on environment and development (unced), SpringerReference. (2011). [https://doi.org/10.1007/springerreference\\_29770](https://doi.org/10.1007/springerreference_29770).
- [19] T. Kan, Sustainable Energy Production from Distributed Renewable Waste Resources through Major Waste-to-Energy Activities, in: *Renew. Energy Syst. from Biomass*, CRC

- Press, Boca Raton: Taylor & Francis, 2019., n.d.: pp. 35–55. <https://doi.org/10.1201/9781315153971-3>.
- [20] D.V. Jackson, Waste recycling and pollution control handbook, *Conserv. Recycl.* 4 (1981) 62–63. [https://doi.org/10.1016/0361-3658\(81\)90010-2](https://doi.org/10.1016/0361-3658(81)90010-2).
- [21] Solid Waste, Hazardous Materials, and Hazardous Waste Management, in: *Best Pract. Environ. Heal.*, Routledge, Boca Raton, FL: CRC Press, 2017: pp. 445–528. <https://doi.org/10.1201/9781315119274-12>.
- [22] A. Sayigh, World renewable energy, *Proc. 3rd World Conf. Photovolt. Energy Convers. C* (2003) 2556–2561. [https://doi.org/10.1016/S0960-1481\(01\)00159-8](https://doi.org/10.1016/S0960-1481(01)00159-8).
- [23] Climate Change and Renewable Energy, in: 2014: pp. 201–210. <https://doi.org/10.1201/b16693-21>.
- [24] COMPOSITES EUROPE 2013 – Facts & Figures, *Reinf. Plast.* 57 (2013) 42. [https://doi.org/10.1016/S0034-3617\(13\)70155-3](https://doi.org/10.1016/S0034-3617(13)70155-3).
- [25] M. Biron, Renewable Plastics Derived From Natural Polymers, in: *Ind. Appl. Renew. Plast.*, Elsevier, 2017: pp. 115–154. <https://doi.org/10.1016/B978-0-323-48065-9.00004-2>.
- [26] [https://www.researchgate.net/figure/The-composition-of-municipal-plastic-waste\\_tbl1\\_327572333](https://www.researchgate.net/figure/The-composition-of-municipal-plastic-waste_tbl1_327572333) (at 15 August 2020)
- [27] D. Briassoulis, M. Hiskakis, E. Babou, S.K. Antiohos, C. Papadi, Experimental investigation of the quality characteristics of agricultural plastic wastes regarding their recycling and energy recovery potential, *Waste Manag.* 32 (2012) 1075–1090. <https://doi.org/10.1016/j.wasman.2012.01.018>.
- [28] T.A. TOMASZEWSKI, Waste Receiving and Processing (WRAP) Facility Final Safety Analysis Report (FSAR), Richland, WA, 2000. <https://doi.org/10.2172/803052>.
- [29] A.S.M.A. Awal, I.A. Shehu, M. Ismail, Effect of cooling regime on the residual performance of high-volume palm oil fuel ash concrete exposed to high temperatures, *Constr. Build. Mater.* 98 (2015) 875–883. <https://doi.org/10.1016/j.conbuildmat.2015.09.001>.
- [30] T. Nomiyama, N. Aihara, A. Chitose, M. Yamada, S. Tojo, Biomass as Local Resource, in: *Res. Approaches to Sustain. Biomass Syst.*, Elsevier, 2014: pp. 7–17. <https://doi.org/10.1016/B978-0-12-404609-2.00002-7>.
- [31] L. Emami Taba, M.F. Irfan, W.A.M. Wan Daud, M.H. Chakrabarti, The effect of temperature on various parameters in coal, biomass and CO-gasification: A review, *Renew. Sustain. Energy Rev.* 16 (2012) 5584–5596. <https://doi.org/10.1016/j.rser.2012.06.015>.
- [32] Lignocellulose Biorefinery, in: *Fungi Lignocellul. Biomass*, Wiley-Blackwell, Oxford, UK, 2012: pp. 201–227. <https://doi.org/10.1002/9781118414514.ch11>.
- [33] C.H. Pang, E. Lester, T. Wu, Influence of lignocellulose and plant cell walls on biomass char morphology and combustion reactivity, *Biomass and Bioenergy.* 119 (2018) 480–491. <https://doi.org/10.1016/j.biombioe.2018.10.011>.
- [34] A.Y. Krylova, V.M. Zaitchenko, Hydrothermal Carbonization of Biomass: A Review, *Solid Fuel Chem.* 52 (2018) 91–103. <https://doi.org/10.3103/S0361521918020076>.
- [35] A. Nzihou, Waste and Biomass Valorization, *Waste and Biomass Valorization.* 1 (2010) 1–2. <https://doi.org/10.1007/s12649-010-9013-y>.
- [36] G. Forsberg, Biomass energy transport, *Biomass and Bioenergy.* 19 (2000) 17–30. [https://doi.org/10.1016/S0961-9534\(00\)00020-9](https://doi.org/10.1016/S0961-9534(00)00020-9).
- [37] 21st European Biomass Conference, *Biomass and Bioenergy.* 65 (2014) 1–2. <https://doi.org/10.1016/j.biombioe.2014.05.009>.

- [38] M. Parikka, Global biomass fuel resources, *Biomass and Bioenergy*. 27 (2004) 613–620. <https://doi.org/10.1016/j.biombioe.2003.07.005>.
- [39] M. Balat, Use of biomass sources for energy in Turkey and a view to biomass potential, *Biomass and Bioenergy*. 29 (2005) 32–41. <https://doi.org/10.1016/j.biombioe.2005.02.004>.
- [40] V.I. Kuprianov, P. Arromdee, Combustion of peanut and tamarind shells in a conical fluidized-bed combustor: A comparative study, *Bioresour. Technol.* 140 (2013) 199–210. <https://doi.org/10.1016/j.biortech.2013.04.086>.
- [41] A.A. Salema, F.N. Ani, Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer, *J. Anal. Appl. Pyrolysis*. 96 (2012) 162–172. <https://doi.org/10.1016/j.jaap.2012.03.018>.
- [42] M.F. Irfan, A. Arami-Niya, M.H. Chakrabarti, W.M.A. Wan Daud, M.R. Usman, Kinetics of gasification of coal, biomass and their blends in air (N<sub>2</sub>/O<sub>2</sub>) and different oxy-fuel (O<sub>2</sub>/CO<sub>2</sub>) atmospheres, *Energy*. 37 (2012) 665–672. <https://doi.org/10.1016/j.energy.2011.10.032>.
- [43] J. Lee, Biological conversion of lignocellulosic biomass to ethanol, *J. Biotechnol.* 56 (1997) 1–24. [https://doi.org/10.1016/S0168-1656\(97\)00073-4](https://doi.org/10.1016/S0168-1656(97)00073-4).
- [44] N. Reddy, Y. Yang, Structure and properties of high quality natural cellulose fibers from cornstalks, *Polymer (Guildf)*. 46 (2005) 5494–5500. <https://doi.org/10.1016/j.polymer.2005.04.073>.
- [45] H.J. Jeong, S.S. Park, J. Hwang, Co-gasification of coal–biomass blended char with CO<sub>2</sub> at temperatures of 900–1100 °C, *Fuel*. 116 (2014) 465–470. <https://doi.org/10.1016/j.fuel.2013.08.015>.
- [46] J. Qiu, L. Chen, Q. Zhu, D. Wang, W. Wang, X. Sun, X. Liu, F. Du, Screening natural antioxidants in peanut shell using DPPH–HPLC–DAD–TOF/MS methods, *Food Chem.* 135 (2012) 2366–2371. <https://doi.org/10.1016/j.foodchem.2012.07.042>.
- [47] C.A. Jordan, G. Akay, Effect of CaO on tar production and dew point depression during gasification of fuel cane bagasse in a novel downdraft gasifier, *Fuel Process. Technol.* 106 (2013) 654–660. <https://doi.org/10.1016/j.fuproc.2012.09.061>.
- [48] G. Holzhey, Waste Paper use in the Community as Seen by the Paper Industry, in: *Waste Manag.*, Springer Netherlands, Dordrecht, 1981: pp. 207–216. [https://doi.org/10.1007/978-94-010-9942-4\\_20](https://doi.org/10.1007/978-94-010-9942-4_20).
- [49] H. Zhou, A. Meng, Y. Long, Q. Li, Y. Zhang, Classification and comparison of municipal solid waste based on thermochemical characteristics, *J. Air Waste Manage. Assoc.* 64 (2014) 597–616. <https://doi.org/10.1080/10962247.2013.873094>.
- [50] K. Yamaguchi, An event study on the concealment of the blending ratio of waste paper, *Waste Manag.* 29 (2009) 1491–1494. <https://doi.org/10.1016/j.wasman.2008.11.029>.
- [51] 2. Brief review of the methods of recycling of polyurethane foam wastes, in: *Recycl. Polyurethane Wastes*, De Gruyter, Berlin, Boston, 2019: pp. 11–34. <https://doi.org/10.1515/9783110641592-002>.
- [52] *Feedstock Recycling of Plastic Wastes*, Royal Society of Chemistry, Cambridge, 1999. <https://doi.org/10.1039/9781847550804>.
- [53] M. El-Fadel, A.N. Findikakis, J.O. Leckie, Environmental Impacts of Solid Waste Landfilling, *J. Environ. Manage.* 50 (1997) 1–25. <https://doi.org/10.1006/jema.1995.0131>.
- [54] M. El-Fadel, A.N. Findikakis, J.O. Leckie, Gas simulation models for solid waste landfills, *Crit. Rev. Environ. Sci. Technol.* 27 (1997) 237–283. <https://doi.org/10.1080/10643389709388500>.
- [55] R. Cossu, R. Stegmann, Waste Management Strategies and Role of Landfilling, in: *Solid*

- Waste Landfilling, Elsevier, 2018: pp. 3–13. <https://doi.org/10.1016/B978-0-12-407721-8.00001-2>.
- [56] H.-J. Ehrig, R. Stegmann, Leachate Quality, in: *Solid Waste Landfilling*, Elsevier, 2018: pp. 511–539. <https://doi.org/10.1016/B978-0-12-407721-8.00026-7>.
- [57] R. Cossu, L. Morello, R. Stegmann, Biochemical Processes in Landfill, in: *Solid Waste Landfilling*, Elsevier, 2018: pp. 91–115. <https://doi.org/10.1016/B978-0-12-407721-8.00006-1>.
- [58] A. Feil, T. Pretz, Mechanical recycling of packaging waste, in: *Plast. Waste Recycl.*, Elsevier, 2020: pp. 283–319. <https://doi.org/10.1016/B978-0-12-817880-5.00011-6>.
- [59] F. Perugini, M.L. Mastellone, U. Arena, A life cycle assessment of mechanical and feedstock recycling options for management of plastic packaging wastes, *Environ. Prog.* 24 (2005) 137–154. <https://doi.org/10.1002/ep.10078>.
- [60] Y.-B. Zhao, X.-D. Lv, H.-G. Ni, Solvent-based separation and recycling of waste plastics: A review, *Chemosphere.* 209 (2018) 707–720. <https://doi.org/10.1016/j.chemosphere.2018.06.095>.
- [61] O. Hjelm, Disposal strategies for municipal solid waste incineration residues, *J. Hazard. Mater.* 47 (1996) 345–368. [https://doi.org/10.1016/0304-3894\(95\)00111-5](https://doi.org/10.1016/0304-3894(95)00111-5).
- [62] A Burning Issue, in: *Chinese Environ. Contention*, Amsterdam University Press, 2019: pp. 53–86. <https://doi.org/10.2307/j.ctvr0qr87.6>.
- [63] B.-H. Kim, S.-J. Lee, S.-J. Mun, Y.-S. Chang, A case study of dioxin monitoring in and around an industrial waste incinerator in Korea, *Chemosphere.* 58 (2005) 1589–1599. <https://doi.org/10.1016/j.chemosphere.2004.10.041>.
- [64] C.-Y. WU, P. BISWAS, N.J. FENDINGER, Model to Assess Heavy Metal Emission from Municipal Solid Waste Incineration, *Hazard. Waste Hazard. Mater.* 11 (1994) 71–92. <https://doi.org/10.1089/hwm.1994.11.71>.
- [65] M.J. Quina, J.C.M. Bordado, R.M. Quinta-Ferreira, Chemical stabilization of air pollution control residues from municipal solid waste incineration, *J. Hazard. Mater.* 179 (2010) 382–392. <https://doi.org/10.1016/j.jhazmat.2010.03.016>.
- [66] Y. Kalmykova, K. Karlfeldt Fedje, Phosphorus recovery from municipal solid waste incineration fly ash, *Waste Manag.* 33 (2013) 1403–1410. <https://doi.org/10.1016/j.wasman.2013.01.040>.
- [67] O. Hjelm, A. Johnson, R. Comans, Incineration: Solid Residues, in: *Solid Waste Technol. Manag.*, John Wiley & Sons, Ltd, Chichester, UK, 2010: pp. 430–462. <https://doi.org/10.1002/9780470666883.ch29>.
- [68] *Gasification of Waste Materials*, Elsevier, 2018. <https://doi.org/10.1016/C2015-0-06162-7>.
- [69] Z.-S. Liu, C.-L. Lin, T.-J. Chang, W.-C. Weng, Waste-gasification efficiency of a two-stage fluidized-bed gasification system, *Waste Manag.* 48 (2016) 250–256. <https://doi.org/10.1016/j.wasman.2015.12.001>.
- [70] Gasification of solid waste: From flue gas to fuel gas technology, *Waste Manag.* 31 (2011) 402. <https://doi.org/10.1016/j.wasman.2010.11.012>.
- [71] U. Arena, Gasification: An alternative solution for waste treatment with energy recovery, *Waste Manag.* 31 (2011) 405–406. <https://doi.org/10.1016/j.wasman.2010.12.006>.
- [72] J.G. Speight, The Fischer–Tropsch Process, in: *Gasif. Unconv. Feed.*, Elsevier, 2014: pp. 118–134. <https://doi.org/10.1016/B978-0-12-799911-1.00005-4>.
- [73] M. Morris, L. Waldheim, Energy recovery from solid waste fuels using advanced gasification technology, *Waste Manag.* 18 (1998) 557–564. [https://doi.org/10.1016/S0956-053X\(98\)00146-9](https://doi.org/10.1016/S0956-053X(98)00146-9).

- [74] J. Scheirs, Overview of Commercial Pyrolysis Processes for Waste Plastics, in: *Feed. Recycl. Pyrolysis Waste Plast.*, John Wiley & Sons, Ltd, Chichester, UK, 2006: pp. 381–433. <https://doi.org/10.1002/0470021543.ch15>.
- [75] A.I. Moreno, R. Font, Pyrolysis of furniture wood waste: Decomposition and gases evolved, *J. Anal. Appl. Pyrolysis.* 113 (2015) 464–473. <https://doi.org/10.1016/j.jaap.2015.03.008>.
- [76] P.T. Williams, Yield and Composition of Gases and Oils/Waxes from the Feedstock Recycling of Waste Plastic, in: *Feed. Recycl. Pyrolysis Waste Plast.*, John Wiley & Sons, Ltd, Chichester, UK, 2006: pp. 285–313. <https://doi.org/10.1002/0470021543.ch11>.
- [77] T. Ademiluyi, T. Adebayo, Fuel gases from pyrolysis of waste Polyethylene sachets, *J. Appl. Sci. Environ. Manag.* 11 (2010). <https://doi.org/10.4314/jasem.v11i2.54979>.
- [78] Y. Xingzhong, Converting Waste Plastics into Liquid Fuel by Pyrolysis: Developments in China, in: *Feed. Recycl. Pyrolysis Waste Plast.*, John Wiley & Sons, Ltd, Chichester, UK, 2006: pp. 729–755. <https://doi.org/10.1002/0470021543.ch28>.
- [79] Chapter 5 Selected applications of analytical pyrolysis in the study of synthetic polymers, in: 2005: pp. 171–182. [https://doi.org/10.1016/S0167-9244\(05\)80006-X](https://doi.org/10.1016/S0167-9244(05)80006-X).
- [80] K. Chan, Pyrolysis studies of synthetic polymers by mass spectrometry and other methods, The University of Hong Kong, 1984. [https://doi.org/10.5353/th\\_b3123022](https://doi.org/10.5353/th_b3123022).
- [81] Chapter 4 Information generated from analytical pyrolysis studies, in: 2005: pp. 145–169. [https://doi.org/10.1016/S0167-9244\(05\)80005-8](https://doi.org/10.1016/S0167-9244(05)80005-8).
- [82] Y. Xue, Thermochemical conversion of organic and plastic waste materials through pyrolysis, Iowa State University, Digital Repository, 2017. <https://doi.org/10.31274/etd-180810-5871>.
- [83] A.Y. Bilgesü, M.Ç. Koçak, A. Karaduman, Waste Plastic Pyrolysis in Free-Fall Reactors, in: *Feed. Recycl. Pyrolysis Waste Plast.*, John Wiley & Sons, Ltd, Chichester, UK, 2006: pp. 605–623. <https://doi.org/10.1002/0470021543.ch23>.
- [84] H. Liu, C. Wang, J. Zhang, W. Zhao, M. Fan, Pyrolysis Kinetics and Thermodynamics of Typical Plastic Waste, *Energy & Fuels.* 34 (2020) 2385–2390. <https://doi.org/10.1021/acs.energyfuels.9b04152>.
- [85] D. Almeida, ed., Thermal and Catalytic Pyrolysis of Plastic Waste, in: *Thermochem. Waste Treat.*, Apple Academic Press, 2016: pp. 133–154. <https://doi.org/10.1201/b19938-12>.
- [86] D. Almeida, M.D.F. Marques, Thermal and Catalytic Pyrolysis of Plastic Waste, in: *Thermochem. Waste Treat.*, Apple Academic Press, Toronto; Waretown, New Jersey : Apple Academic Press, 2016. |, 2017: pp. 133–153. <https://doi.org/10.1201/b19938-12>.
- [87] S. Thangalazhy-Gopakumar, S. Adhikari, R.B. Gupta, S.D. Fernando, Influence of Pyrolysis Operating Conditions on Bio-Oil Components: A Microscale Study in a Pyroprobe, *Energy & Fuels.* 25 (2011) 1191–1199. <https://doi.org/10.1021/ef101032s>.
- [88] Effects of Heating Rate and Particle Size on Pyrolysis Kinetics of Mengen Lignite, *Energy Sources.* 23 (2001) 337–344. <https://doi.org/10.1080/009083101300110887>.
- [89] J. Lédé, O. Authier, Temperature and heating rate of solid particles undergoing a thermal decomposition. Which criteria for characterizing fast pyrolysis?, *J. Anal. Appl. Pyrolysis.* 113 (2015) 1–14. <https://doi.org/10.1016/j.jaap.2014.11.013>.
- [90] A. Oasmaa, D.C. Elliott, J. Korhonen, Acidity of Biomass Fast Pyrolysis Bio-oils, *Energy & Fuels.* 24 (2010). <https://doi.org/10.1021/ef100935r>.
- [91] M. Radovanovic, Some remarks on the viscosity measurement of pyrolysis liquids, *Biomass and Bioenergy.* 18 (2000) 209–222. [https://doi.org/10.1016/S0961-9534\(99\)00082-3](https://doi.org/10.1016/S0961-9534(99)00082-3).



- [92] T. Murae, Characterization of extraterrestrial high-molecular-weight organic matter by pyrolysis-gas chromatography/mass spectrometry, *J. Anal. Appl. Pyrolysis*. 32 (1995) 65–73. [https://doi.org/10.1016/0165-2370\(94\)00871-W](https://doi.org/10.1016/0165-2370(94)00871-W).
- [93] Q. Huang, C. Liu, R. Wei, J. Wang, Experimental study of polyethylene pyrolysis and combustion over HZSM-5, HUSY, and MCM-41, *J. Hazard. Mater.* 333 (2017) 10–22. <https://doi.org/10.1016/j.jhazmat.2017.03.029>.
- [94] A. Marcilla, M.I. Beltrán, R. Navarro, Effect of regeneration temperature and time on the activity of HUSY and HZSM5 zeolites during the catalytic pyrolysis of polyethylene, *J. Anal. Appl. Pyrolysis*. 74 (2005) 361–369. <https://doi.org/10.1016/j.jaap.2004.10.006>.
- [95] Y. Chi, J. Xue, J. Zhuo, D. Zhang, M. Liu, Q. Yao, Catalytic co-pyrolysis of cellulose and polypropylene over all-silica mesoporous catalyst MCM-41 and Al-MCM-41, *Sci. Total Environ.* 633 (2018) 1105–1113. <https://doi.org/10.1016/j.scitotenv.2018.03.239>.
- [96] L. Heller-Kallai, I. Miloslavski, Z. Aizenshtat, Volatile products of clay mineral pyrolysis revealed by their effect on calcite, *Clay Miner.* 22 (1987) 339–348. <https://doi.org/10.1180/claymin.1987.022.3.08>.
- [97] Z. Demrew Yigezu, K. Muthukumar, Structural characteristics of selected metal oxides used for the catalytic pyrolysis of sunflower oil, *J. Anal. Appl. Pyrolysis*. 114 (2015) 60–67. <https://doi.org/10.1016/j.jaap.2015.05.002>.
- [98] P. Pánek, B. Kostura, I. Čepeláková, I. Koutník, T. Tomšej, Pyrolysis of oil sludge with calcium-containing additive, *J. Anal. Appl. Pyrolysis*. 108 (2014) 274–283. <https://doi.org/10.1016/j.jaap.2014.04.005>.
- [99] Z.Z. Hlaing, T. Wajima, S. Uchiyama, H. Nakagome, Reduction of Bromine Compounds in the Pyrolysis Oil of Computer Casing Plastics Using Shell, Ca(OH)<sub>2</sub> and NaOH, *APCBEE Procedia*. 10 (2014) 193–197. <https://doi.org/10.1016/j.apcbee.2014.10.037>.
- [100] Abdullah, M. Apriyanti, Sunardi, U.T. Santoso, A.B. Junaidi, D. Aditiya, U. Irawati, Pyrolysis of palm oil using zeolite catalyst and characterization of the boil-oil, *Green Process. Synth.* 8 (2019) 649–658. <https://doi.org/10.1515/gps-2019-0035>.
- [101] K.-H. Lee, Effects of the types of zeolites on catalytic upgrading of pyrolysis wax oil, *J. Anal. Appl. Pyrolysis*. 94 (2012) 209–214. <https://doi.org/10.1016/j.jaap.2011.12.015>.
- [102] S.R. Naqvi, Y. Uemura, S. Yusup, Y. Sugiur, N. Nishiyama, M. Naqvi, The Role of Zeolite Structure and Acidity in Catalytic Deoxygenation of Biomass Pyrolysis Vapors, *Energy Procedia*. 75 (2015) 793–800. <https://doi.org/10.1016/j.egypro.2015.07.126>.
- [103] I. Ahmad, M. Ismail Khan, M. Ishaq, H. Khan, K. Gul, W. Ahmad, Catalytic efficiency of some novel nanostructured heterogeneous solid catalysts in pyrolysis of HDPE, *Polym. Degrad. Stab.* 98 (2013) 2512–2519. <https://doi.org/10.1016/j.polymdegradstab.2013.09.009>.
- [104] P.T. Williams, E.A. Williams, Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock, *J. Anal. Appl. Pyrolysis*. 51 (1999) 107–126. [https://doi.org/10.1016/S0165-2370\(99\)00011-X](https://doi.org/10.1016/S0165-2370(99)00011-X).
- [105] Y.-H. Seo, K.-H. Lee, D.-H. Shin, Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis, *J. Anal. Appl. Pyrolysis*. 70 (2003) 383–398. [https://doi.org/10.1016/S0165-2370\(02\)00186-9](https://doi.org/10.1016/S0165-2370(02)00186-9).
- [106] Y. Sakata, M.A. Uddin, A. Muto, Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts, *J. Anal. Appl. Pyrolysis*. 51 (1999) 135–155. [https://doi.org/10.1016/S0165-2370\(99\)00013-3](https://doi.org/10.1016/S0165-2370(99)00013-3).
- [107] H. Bockhorn, A. Hornung, U. Hornung, S. Teepe, J. Weichmann, Investigation of the Kinetics of Thermal Degradation of Commodity Plastics, *Combust. Sci. Technol.* 116–117 (1996) 129–151. <https://doi.org/10.1080/00102209608935546>.
- [108] D.S. Scott, S.R. Czernik, J. Piskorz, D.S.A.G. Radlein, Fast pyrolysis of plastic wastes,

- Energy & Fuels. 4 (1990) 407–411. <https://doi.org/10.1021/ef00022a013>.
- [109] P.T. Williams, E.A. Williams, Interaction of Plastics in Mixed-Plastics Pyrolysis, *Energy & Fuels*. 13 (1999) 188–196. <https://doi.org/10.1021/ef980163x>.
- [110] X. Wang, Q. Jin, J. Zhang, Y. Li, S. Li, H. Mikulčić, M. Vujanović, H. Tan, N. Duić, Soot formation during polyurethane (PU) plastic pyrolysis: The effects of temperature and volatile residence time, *Energy Convers. Manag.* 164 (2018) 353–362. <https://doi.org/10.1016/j.enconman.2018.02.082>.
- [111] M. Syamsiro, H. Saptoadi, T. Norsujianto, P. Noviasri, S. Cheng, Z. Alimuddin, K. Yoshikawa, Fuel Oil Production from Municipal Plastic Wastes in Sequential Pyrolysis and Catalytic Reforming Reactors, *Energy Procedia*. 47 (2014) 180–188. <https://doi.org/10.1016/j.egypro.2014.01.212>.
- [112] I. Ahmad, M.I. Khan, H. Khan, M. Ishaq, R. Tariq, K. Gul, W. Ahmad, Pyrolysis Study of Polypropylene and Polyethylene Into Premium Oil Products, *Int. J. Green Energy*. 12 (2015) 663–671. <https://doi.org/10.1080/15435075.2014.880146>.
- [113] A. Marcilla, M.I. Beltrán, R. Navarro, Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions, *Appl. Catal. B Environ.* 86 (2009) 78–86. <https://doi.org/10.1016/j.apcatb.2008.07.026>.
- [114] Y. Sakata, M.A. Uddin, A. Muto, Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts, *J. Anal. Appl. Pyrolysis*. 51 (1999) 135–155. [https://doi.org/10.1016/S0165-2370\(99\)00013-3](https://doi.org/10.1016/S0165-2370(99)00013-3).
- [115] S.M. FakhrHoseini, M. Dastanian, Predicting Pyrolysis Products of PE, PP, and PET Using NRTL Activity Coefficient Model, *J. Chem.* 2013 (2013) 1–5. <https://doi.org/10.1155/2013/487676>.
- [116] A. Demirbas, Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons, *J. Anal. Appl. Pyrolysis*. 72 (2004) 97–102. <https://doi.org/10.1016/j.jaap.2004.03.001>.
- [117] J.A. Onwudili, N. Insura, P.T. Williams, Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time, *J. Anal. Appl. Pyrolysis*. 86 (2009) 293–303. <https://doi.org/10.1016/j.jaap.2009.07.008>.
- [118] F.-X. Collard, J. Blin, A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin, *Renew. Sustain. Energy Rev.* 38 (2014) 594–608. <https://doi.org/10.1016/j.rser.2014.06.013>.
- [119] G. WANG, W. LI, B. LI, H. CHEN, TG study on pyrolysis of biomass and its three components under syngas☆, *Fuel*. 87 (2008) 552–558. <https://doi.org/10.1016/j.fuel.2007.02.032>.
- [120] F. Yan, S. Luo, Z. Hu, B. Xiao, G. Cheng, Hydrogen-rich gas production by steam gasification of char from biomass fast pyrolysis in a fixed-bed reactor: Influence of temperature and steam on hydrogen yield and syngas composition, *Bioresour. Technol.* 101 (2010) 5633–5637. <https://doi.org/10.1016/j.biortech.2010.02.025>.
- [121] J. Lehto, A. Oasmaa, Y. Solantausta, M. Kytö, D. Chiaramonti, Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass, *Appl. Energy*. 116 (2014) 178–190. <https://doi.org/10.1016/j.apenergy.2013.11.040>.
- [122] M. García-Pérez, A. Chaala, H. Pakdel, D. Kretschmer, D. Rodrigue, C. Roy, Multiphase Structure of Bio-oils, *Energy & Fuels*. 20 (2006) 364–375. <https://doi.org/10.1021/ef050248f>.
- [123] S. Kersten, M. Garcia-Perez, Recent developments in fast pyrolysis of ligno-cellulosic materials, *Curr. Opin. Biotechnol.* 24 (2013) 414–420.

<https://doi.org/10.1016/j.copbio.2013.04.003>.

- [124] G.J.S. Dawes, E.L. Scott, J. Le Nôtre, J.P.M. Sanders, J.H. Bitter, Deoxygenation of biobased molecules by decarboxylation and decarbonylation – a review on the role of heterogeneous, homogeneous and bio-catalysis, *Green Chem.* 17 (2015) 3231–3250. <https://doi.org/10.1039/C5GC00023H>.
- [125] J. Akhtar, N.A.S. Amin, A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass, *Renew. Sustain. Energy Rev.* 15 (2011) 1615–1624. <https://doi.org/10.1016/j.rser.2010.11.054>.
- [126] H. Wang, J. Male, Y. Wang, Recent Advances in Hydrotreating of Pyrolysis Bio-Oil and Its Oxygen-Containing Model Compounds, *ACS Catal.* 3 (2013) 1047–1070. <https://doi.org/10.1021/cs400069z>.
- [127] T. Cornelissen, J. Yperman, G. Reggers, S. Schreurs, R. Carleer, Flash co-pyrolysis of biomass with polylactic acid. Part 1: Influence on bio-oil yield and heating value, *Fuel.* 87 (2008) 1031–1041. <https://doi.org/10.1016/j.fuel.2007.07.019>.
- [128] 4. Pyrolysis of lignin, in: *Pyrolysis of Biomass*, De Gruyter, Berlin, Boston, 2016. <https://doi.org/10.1515/9783110369632-006>.
- [129] Y.-F. Huang, P.-T. Chiueh, W.-H. Kuan, S.-L. Lo, Product distribution and heating performance of lignocellulosic biomass pyrolysis using microwave heating, *Energy Procedia.* 152 (2018) 910–915. <https://doi.org/10.1016/j.egypro.2018.09.092>.
- [130] J. V. Ortega, A.M. Renehan, M.W. Liberatore, A.M. Herring, Physical and chemical characteristics of aging pyrolysis oils produced from hardwood and softwood feedstocks, *J. Anal. Appl. Pyrolysis.* 91 (2011) 190–198. <https://doi.org/10.1016/j.jaap.2011.02.007>.
- [131] F.A. Agblevor, S. Beis, S.S. Kim, R. Tarrant, N.O. Mante, Biocrude oils from the fast pyrolysis of poultry litter and hardwood, *Waste Manag.* 30 (2010) 298–307. <https://doi.org/10.1016/j.wasman.2009.09.042>.
- [132] M. García-Pérez, A. Chaala, H. Pakdel, D. Kretschmer, C. Roy, Vacuum pyrolysis of softwood and hardwood biomass, *J. Anal. Appl. Pyrolysis.* 78 (2007) 104–116. <https://doi.org/10.1016/j.jaap.2006.05.003>.
- [133] M. García-Pérez, A. Chaala, H. Pakdel, D. Kretschmer, C. Roy, Vacuum pyrolysis of softwood and hardwood biomass. Comparison between product yields and bio-oil properties, *J. Anal. Appl. Pyrolysis.* 78 (2007) 104–116. <https://doi.org/10.1016/j.jaap.2006.05.003>.
- [134] M.F. Demirbas, Characterization of Bio-oils from Spruce Wood (*Picea orientalis* L.) via Pyrolysis, *Energy Sources, Part A Recover. Util. Environ. Eff.* 32 (2010) 909–916. <https://doi.org/10.1080/15567030903059970>.
- [135] A. Shah, M.J. Darr, D. Dalluge, D. Medic, K. Webster, R.C. Brown, Physicochemical properties of bio-oil and biochar produced by fast pyrolysis of stored single-pass corn stover and cobs, *Bioresour. Technol.* 125 (2012) 348–352. <https://doi.org/10.1016/j.biortech.2012.09.061>.
- [136] J.A. Capunitan, S.C. Capareda, Assessing the potential for biofuel production of corn stover pyrolysis using a pressurized batch reactor, *Fuel.* 95 (2012) 563–572. <https://doi.org/10.1016/j.fuel.2011.12.029>.
- [137] T. Ding, S. Li, J. Xie, W. Song, J. Yao, W. Lin, Rapid Pyrolysis of Wheat Straw in a Bench-Scale Circulating Fluidized-Bed Downer Reactor, *Chem. Eng. Technol.* 35 (2012) 2170–2176. <https://doi.org/10.1002/ceat.201200140>.
- [138] A.E. Pütün, E. Apaydin, E. Pütün, Bio-oil production from pyrolysis and steam pyrolysis of soybean-cake: product yields and composition, *Energy.* 27 (2002) 703–713. [https://doi.org/10.1016/S0360-5442\(02\)00015-4](https://doi.org/10.1016/S0360-5442(02)00015-4).
- [139] T. Imam, S. Capareda, Characterization of bio-oil, syn-gas and bio-char from switchgrass

- pyrolysis at various temperatures, *J. Anal. Appl. Pyrolysis*. 93 (2012) 170–177. <https://doi.org/10.1016/j.jaap.2011.11.010>.
- [140] A.A. Boateng, D.E. Daugaard, N.M. Goldberg, K.B. Hicks, Bench-Scale Fluidized-Bed Pyrolysis of Switchgrass for Bio-Oil Production †, *Ind. Eng. Chem. Res.* 46 (2007) 1891–1897. <https://doi.org/10.1021/ie0614529>.
- [141] S. Şensöz, İ. Kaynar, Bio-oil production from soybean (*Glycine max L.*); fuel properties of Bio-oil, *Ind. Crops Prod.* 23 (2006) 99–105. <https://doi.org/10.1016/j.indcrop.2005.04.005>.
- [142] B.B. Uzun, A.E. Pütün, E. Pütün, Fast pyrolysis of soybean cake: Product yields and compositions, *Bioresour. Technol.* 97 (2006) 569–576. <https://doi.org/10.1016/j.biortech.2005.03.026>.
- [143] C.A. Mullen, A.A. Boateng, N.M. Goldberg, I.M. Lima, D.A. Laird, K.B. Hicks, Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, *Biomass and Bioenergy*. 34 (2010) 67–74. <https://doi.org/10.1016/j.biombioe.2009.09.012>.
- [144] Y. Chen, D.R.U. Knappe, M.A. Barlaz, Effect of Cellulose/Hemicellulose and Lignin on the Bioavailability of Toluene Sorbed to Waste Paper, *Environ. Sci. Technol.* 38 (2004) 3731–3736. <https://doi.org/10.1021/es035286x>.
- [145] J. Pérez, J. Muñoz-Dorado, T. de la Rubia, J. Martínez, Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview, *Int. Microbiol.* 5 (2002) 53–63. <https://doi.org/10.1007/s10123-002-0062-3>.
- [146] L. Li, H. Zhang, X. Zhuang, Pyrolysis of Waste Paper: Characterization and Composition of Pyrolysis Oil, *Energy Sources*. 27 (2005) 867–873. <https://doi.org/10.1080/00908310490450872>.
- [147] M. Serio, E. Kroo, E. Florczak, M. Wójtowicz, K. Wignarajah, J. Hogan, J. Fisher, Pyrolysis of Mixed Solid Food, Paper, and Packaging Wastes, in: 2008. <https://doi.org/10.4271/2008-01-2050>.
- [148] D. Czajczyńska, L. Anguilano, H. Ghazal, R. Krzyżyńska, A.J. Reynolds, N. Spencer, H. Jouhara, Potential of pyrolysis processes in the waste management sector, *Therm. Sci. Eng. Prog.* 3 (2017) 171–197. <https://doi.org/10.1016/j.tsep.2017.06.003>.
- [149] V. Strezov, T.J. Evans, Thermal processing of paper sludge and characterisation of its pyrolysis products, *Waste Manag.* 29 (2009) 1644–1648. <https://doi.org/10.1016/j.wasman.2008.11.024>.
- [150] E.M. Grieco, G. Baldi, Pyrolysis of polyethylene mixed with paper and wood: Interaction effects on tar, char and gas yields, *Waste Manag.* 32 (2012) 833–839. <https://doi.org/10.1016/j.wasman.2011.12.014>.
- [151] B. Biswal, S. Kumar, R.K. Singh, Production of Hydrocarbon Liquid by Thermal Pyrolysis of Paper Cup Waste, *J. Waste Manag.* 2013 (2013) 1–7. <https://doi.org/10.1155/2013/731858>.
- [152] P. Devi, A.K. Saroha, Effect of pyrolysis temperature on polycyclic aromatic hydrocarbons toxicity and sorption behaviour of biochars prepared by pyrolysis of paper mill effluent treatment plant sludge, *Bioresour. Technol.* 192 (2015) 312–320. <https://doi.org/10.1016/j.biortech.2015.05.084>.
- [153] Z. Zhang, D.J. Macquarrie, M. De bruyn, V.L. Budarin, A.J. Hunt, M.J. Gronnow, J. Fan, P.S. Shuttleworth, J.H. Clark, A.S. Matharu, Low-temperature microwave-assisted pyrolysis of waste office paper and the application of bio-oil as an Al adhesive, *Green Chem.* 17 (2015) 260–270. <https://doi.org/10.1039/C4GC00768A>.
- [154] R. Lou, S. Wu, G. Lv, Q. Yang, Energy and resource utilization of deinking sludge pyrolysis, *Appl. Energy*. 90 (2012) 46–50. <https://doi.org/10.1016/j.apenergy.2010.12.025>.

- [155] H. Vuthaluru, Thermal behaviour of coal/biomass blends during co-pyrolysis, *Fuel Process. Technol.* 85 (2004) 141–155. [https://doi.org/10.1016/S0378-3820\(03\)00112-7](https://doi.org/10.1016/S0378-3820(03)00112-7).
- [156] M. Brebu, S. Ucar, C. Vasile, J. Yanik, Co-pyrolysis of pine cone with synthetic polymers, *Fuel*. 89 (2010) 1911–1918. <https://doi.org/10.1016/j.fuel.2010.01.029>.
- [157] F. Abnisa, W.M.A. Wan Daud, A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil, *Energy Convers. Manag.* 87 (2014) 71–85. <https://doi.org/10.1016/j.enconman.2014.07.007>.
- [158] A.-G. Collot, Y. Zhuo, D. Dugwell, R. Kandiyoti, Co-pyrolysis and co-gasification of coal and biomass in bench-scale fixed-bed and fluidised bed reactors, *Fuel*. 78 (1999) 667–679. [https://doi.org/10.1016/S0016-2361\(98\)00202-6](https://doi.org/10.1016/S0016-2361(98)00202-6).
- [159] S. Krerkkaiwan, C. Fushimi, A. Tsutsumi, P. Kuchonthara, Synergetic effect during co-pyrolysis/gasification of biomass and sub-bituminous coal, *Fuel Process. Technol.* 115 (2013) 11–18. <https://doi.org/10.1016/j.fuproc.2013.03.044>.
- [160] T. Sonobe, N. Worasuwannarak, S. Pipatmanomai, Synergies in co-pyrolysis of Thai lignite and corncob, *Fuel Process. Technol.* 89 (2008) 1371–1378. <https://doi.org/10.1016/j.fuproc.2008.06.006>.
- [161] T. Cornelissen, M. Jans, J. Yperman, G. Reggers, S. Schreurs, R. Carleer, Flash co-pyrolysis of biomass with polyhydroxybutyrate: Part 1. Influence on bio-oil yield, water content, heating value and the production of chemicals, *Fuel*. 87 (2008) 2523–2532. <https://doi.org/10.1016/j.fuel.2008.02.024>.
- [162] T. Cornelissen, G. Molenberghs, M. Jans, J. Yperman, S. Schreurs, R. Carleer, A statistical data-processing methodology of Py–GC/MS data for the simulation of flash co-pyrolysis reactor experiments, *Chemom. Intell. Lab. Syst.* 110 (2012) 123–128. <https://doi.org/10.1016/j.chemolab.2011.10.011>.
- [163] T. Cornelissen, M. Jans, M. Stals, T. Kuppens, T. Thewys, G.K. Janssens, H. Pastijn, J. Yperman, G. Reggers, S. Schreurs, R. Carleer, Flash co-pyrolysis of biomass: The influence of biopolymers, *J. Anal. Appl. Pyrolysis.* 85 (2009) 87–97. <https://doi.org/10.1016/j.jaap.2008.12.003>.
- [164] Q. Jin, X. Wang, S. Li, H. Mikulčić, T. Bešenić, S. Deng, M. Vujanović, H. Tan, B.M. Kumfer, Synergistic effects during co-pyrolysis of biomass and plastic: Gas, tar, soot, char products and thermogravimetric study, *J. Energy Inst.* 92 (2019) 108–117. <https://doi.org/10.1016/j.joei.2017.11.001>.
- [165] B. Cao, Y. Sun, J. Guo, S. Wang, J. Yuan, S. Esakkimuthu, B. Bernard Uzojinwa, C. Yuan, A.E.-F. Abomohra, L. Qian, L. Liu, B. Li, Z. He, Q. Wang, Synergistic effects of co-pyrolysis of macroalgae and polyvinyl chloride on bio-oil/bio-char properties and transferring regularity of chlorine, *Fuel*. 246 (2019) 319–329. <https://doi.org/10.1016/j.fuel.2019.02.037>.
- [166] Y. Song, N. Yin, D. Yao, Q. Ma, J. Zhou, X. Lan, Co-pyrolysis characteristics and synergistic mechanism of low-rank coal and direct liquefaction residue, *Energy Sources, Part A Recover. Util. Environ. Eff.* 41 (2019) 2675–2689. <https://doi.org/10.1080/15567036.2019.1568639>.
- [167] J. Fei, J. Zhang, F. Wang, J. Wang, Synergistic effects on co-pyrolysis of lignite and high-sulfur swelling coal, *J. Anal. Appl. Pyrolysis.* 95 (2012) 61–67. <https://doi.org/10.1016/j.jaap.2012.01.006>.
- [168] Z. Wu, S. Wang, J. Zhao, L. Chen, H. Meng, Synergistic effect on thermal behavior during co-pyrolysis of lignocellulosic biomass model components blend with bituminous coal, *Bioresour. Technol.* 169 (2014) 220–228. <https://doi.org/10.1016/j.biortech.2014.06.105>.
- [169] X. Zhang, H. Lei, S. Chen, J. Wu, Catalytic co-pyrolysis of lignocellulosic biomass with polymers: a critical review, *Green Chem.* 18 (2016) 4145–4169.

<https://doi.org/10.1039/C6GC00911E>.

- [170] W.-J. Liu, K. Tian, H. Jiang, X.-S. Zhang, G.-X. Yang, Preparation of liquid chemical feedstocks by co-pyrolysis of electronic waste and biomass without formation of polybrominated dibenzo-p-dioxins, *Bioresour. Technol.* 128 (2013) 1–7. <https://doi.org/10.1016/j.biortech.2012.10.160>.
- [171] L. Zhou, Y. Wang, Q. Huang, J. Cai, Thermogravimetric characteristics and kinetic of plastic and biomass blends co-pyrolysis, *Fuel Process. Technol.* 87 (2006) 963–969. <https://doi.org/10.1016/j.fuproc.2006.07.002>.
- [172] Ö. Çepeliogullar, A.E. Pütün, Thermal and kinetic behaviors of biomass and plastic wastes in co-pyrolysis, *Energy Convers. Manag.* 75 (2013) 263–270. <https://doi.org/10.1016/j.enconman.2013.06.036>.
- [173] H. Hassan, J.K. Lim, B.H. Hameed, Recent progress on biomass co-pyrolysis conversion into high-quality bio-oil, *Bioresour. Technol.* 221 (2016) 645–655. <https://doi.org/10.1016/j.biortech.2016.09.026>.
- [174] Y. Matsuzawa, M. Ayabe, J. Nishino, Acceleration of cellulose co-pyrolysis with polymer, *Polym. Degrad. Stab.* 71 (2001) 435–444. [https://doi.org/10.1016/S0141-3910\(00\)00195-6](https://doi.org/10.1016/S0141-3910(00)00195-6).
- [175] Y.M. Kim, J. Jae, B.S. Kim, Y. Hong, S.C. Jung, Y.K. Park, Catalytic co-pyrolysis of torrefied yellow poplar and high-density polyethylene using microporous HZSM-5 and mesoporous Al-MCM-41 catalysts, *Energy Convers. Manag.* 149 (2017) 966–973. <https://doi.org/10.1016/j.enconman.2017.04.033>.
- [176] H. Shafaghat, H.W. Lee, Y.F. Tsang, D. Oh, J. Jae, S.-C. Jung, C.H. Ko, S.S. Lam, Y.-K. Park, In-situ and ex-situ catalytic pyrolysis/co-pyrolysis of empty fruit bunches using mesostructured aluminosilicate catalysts, *Chem. Eng. J.* 366 (2019) 330–338. <https://doi.org/10.1016/j.cej.2019.02.055>.
- [177] W. Chen, S. Shi, J. Zhang, M. Chen, X. Zhou, Co-pyrolysis of waste newspaper with high-density polyethylene: Synergistic effect and oil characterization, *Energy Convers. Manag.* 112 (2016) 41–48. <https://doi.org/10.1016/j.enconman.2016.01.005>.
- [178] P. Leclerc, J. Doucet, J. Chaouki, Development of a microwave thermogravimetric analyzer and its application on polystyrene microwave pyrolysis kinetics, *J. Anal. Appl. Pyrolysis.* 130 (2018) 209–215. <https://doi.org/10.1016/j.jaap.2018.01.008>.
- [179] A. Korkmaz, J. Yanik, M. Brebu, C. Vasile, Pyrolysis of the tetra pak, *Waste Manag.* 29 (2009) 2836–2841. <https://doi.org/10.1016/j.wasman.2009.07.008>.
- [180] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, A. Torres, Pyrolysis of municipal plastic wastes II: Influence of raw material composition under catalytic conditions, *Waste Manag.* 31 (2011) 1973–1983. <https://doi.org/10.1016/j.wasman.2011.05.021>.
- [181] N. Sophonrat, L. Sandström, I.N. Zaini, W. Yang, Stepwise pyrolysis of mixed plastics and paper for separation of oxygenated and hydrocarbon condensates, *Appl. Energy.* 229 (2018) 314–325. <https://doi.org/10.1016/j.apenergy.2018.08.006>.
- [182] L.J. Brown, F.-X. Collard, J. Görgens, Pyrolysis of fibre residues with plastic contamination from a paper recycling mill: Energy recoveries, *Energy Convers. Manag.* 133 (2017) 110–117. <https://doi.org/10.1016/j.enconman.2016.11.065>.
- [183] A. Demetrious, E. Crossin, Life cycle assessment of paper and plastic packaging waste in landfill, incineration, and gasification-pyrolysis, *J. Mater. Cycles Waste Manag.* 21 (2019) 850–860. <https://doi.org/10.1007/s10163-019-00842-4>.
- [184] R.K. Singh, B. Ruj, Time and temperature depended fuel gas generation from pyrolysis of real world municipal plastic waste, *Fuel.* 174 (2016) 164–171. <https://doi.org/10.1016/j.fuel.2016.01.049>.

- [185] A. Veksha, A. Giannis, W.-D. Oh, G. Lisak, Catalytic processing of non-condensable pyrolysis gas from plastics: Effects of calcium supports on nickel-catalyzed decomposition of hydrocarbons and HCl sorption, *Chem. Eng. Sci.* 189 (2018) 311–319. <https://doi.org/10.1016/j.ces.2018.06.014>.
- [186] R. Miranda, H. Pakdel, C. Roy, C. Vasile, Vacuum pyrolysis of commingled plastics containing PVC II. Product analysis, *Polym. Degrad. Stab.* 73 (2001) 47–67. [https://doi.org/10.1016/S0141-3910\(01\)00066-0](https://doi.org/10.1016/S0141-3910(01)00066-0).
- [187] S. Arbogast, D. Bellman, J.D. Paynter, J. Wykowski, Advanced bio-fuels from pyrolysis oil: The impact of economies of scale and use of existing logistic and processing capabilities, *Fuel Process. Technol.* 104 (2012) 121–127. <https://doi.org/10.1016/j.fuproc.2012.04.036>.
- [188] H. Luik, I. Johannes, V. Palu, L. Luik, K. Kruusement, Transformations of biomass internal oxygen at varied pyrolysis conditions, *J. Anal. Appl. Pyrolysis.* 79 (2007) 121–127. <https://doi.org/10.1016/j.jaap.2006.12.028>.
- [189] A. V Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass and Bioenergy.* 38 (2012). <https://doi.org/10.1016/j.biombioe.2011.01.048>.
- [190] Y. Wang, T. He, K. Liu, J. Wu, Y. Fang, From biomass to advanced bio-fuel by catalytic pyrolysis/hydro-processing: Hydrodeoxygenation of bio-oil derived from biomass catalytic pyrolysis, *Bioresour. Technol.* 108 (2012) 280–284. <https://doi.org/10.1016/j.biortech.2011.12.132>.
- [191] J. Fan, T.N. Kalnes, M. Alward, J. Klinger, A. Sadehvandi, D.R. Shonnard, Life cycle assessment of electricity generation using fast pyrolysis bio-oil, *Renew. Energy.* 36 (2011) 632–641. <https://doi.org/10.1016/j.renene.2010.06.045>.
- [192] F. de M. Mercader, M.J. Groeneveld, S.R.A. Kersten, R.H. Venderbosch, J.A. Hogendoorn, Pyrolysis oil upgrading by high pressure thermal treatment, *Fuel.* 89 (2010) 2829–2837. <https://doi.org/10.1016/j.fuel.2010.01.026>.
- [193] K. Sipilä, E. Kuoppala, L. Fagernäs, A. Oasmaa, Characterization of biomass-based flash pyrolysis oils, *Biomass and Bioenergy.* 14 (1998) 103–113. [https://doi.org/10.1016/S0961-9534\(97\)10024-1](https://doi.org/10.1016/S0961-9534(97)10024-1).
- [194] V.A. Doshi, H.B. Vuthaluru, T. Bastow, Investigations into the control of odour and viscosity of biomass oil derived from pyrolysis of sewage sludge, *Fuel Process. Technol.* 86 (2005) 885–897. <https://doi.org/10.1016/j.fuproc.2004.10.001>.
- [195] D. Fu, S. Farag, J. Chaouki, P.G. Jessop, Extraction of phenols from lignin microwave-pyrolysis oil using a switchable hydrophilicity solvent, *Bioresour. Technol.* 154 (2014) 101–108. <https://doi.org/10.1016/j.biortech.2013.11.091>.
- [196] L. Fele Žilnik, A. Jazbinšek, Recovery of renewable phenolic fraction from pyrolysis oil, *Sep. Purif. Technol.* 86 (2012) 157–170. <https://doi.org/10.1016/j.seppur.2011.10.040>.
- [197] A. Khodier, P. Kilgallon, N. Legrave, N. Simms, J. Oakey, T. Bridgwater, Pilot-scale combustion of fast-pyrolysis bio-oil: Ash deposition and gaseous emissions, *Environ. Prog. Sustain. Energy.* 28 (2009) 397–403. <https://doi.org/10.1002/ep.10379>.
- [198] Y. Xue, S. Zhou, R.C. Brown, A. Kelkar, X. Bai, Fast pyrolysis of biomass and waste plastic in a fluidized bed reactor, *Fuel.* 156 (2015) 40–46. <https://doi.org/10.1016/j.fuel.2015.04.033>.
- [199] M.J. Antal, M. Grønli, The Art, Science, and Technology of Charcoal Production †, *Ind. Eng. Chem. Res.* 42 (2003) 1619–1640. <https://doi.org/10.1021/ie0207919>.
- [200] J. Trabalka, Atmospheric carbon dioxide and the global carbon cycle, 1985. <https://doi.org/10.2172/6048470>.
- [201] J. Lehmann, Bio-energy in the black, *Front. Ecol. Environ.* preprint (2007) 1. <https://doi.org/10.1890/060133>.

- [202] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, On the characterization of acidic and basic surface sites on carbons by various techniques, *Carbon* N. Y. 37 (1999) 1215–1221. [https://doi.org/10.1016/S0008-6223\(98\)00317-0](https://doi.org/10.1016/S0008-6223(98)00317-0).
- [203] M.I. Schnitzer, C.M. Monreal, G.A. Facey, P.B. Fransham, The conversion of chicken manure to biooil by fast pyrolysis I. Analyses of chicken manure, biooils and char by <sup>13</sup>C and <sup>1</sup>H NMR and FTIR spectrophotometry, *J. Environ. Sci. Heal. Part B.* 42 (2007) 71–77. <https://doi.org/10.1080/03601230601020894>.
- [204] S. Thangalazhy-Gopakumar, W.M.A. Al-Nadheri, D. Jegarajan, J.N. Sahu, N.M. Mubarak, S. Nizamuddin, Utilization of palm oil sludge through pyrolysis for bio-oil and bio-char production, *Bioresour. Technol.* 178 (2015) 65–69. <https://doi.org/10.1016/j.biortech.2014.09.068>.
- [205] A. Oasmaa, M. Kyt, K. Sipil, Pyrolysis Oil Combustion Tests in an Industrial Boiler, in: *Prog. Thermochem. Biomass Convers.*, Blackwell Science Ltd, Oxford, UK, n.d.: pp. 1468–1481. <https://doi.org/10.1002/9780470694954.ch121>.
- [206] Q. Lu, W.-Z. Li, X.-F. Zhu, Overview of fuel properties of biomass fast pyrolysis oils, *Energy Convers. Manag.* 50 (2009) 1376–1383. <https://doi.org/10.1016/j.enconman.2009.01.001>.
- [207] R. Fahmi, A.V. Bridgwater, I. Donnison, N. Yates, J.M. Jones, The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability, *Fuel.* 87 (2008) 1230–1240. <https://doi.org/10.1016/j.fuel.2007.07.026>.
- [208] J.P. Diebold, A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils, *Energy.* 2 (1999). <https://doi.org/10.2172/753818>.
- [209] M.. Boucher, A. Chaala, H. Pakdel, C. Roy, Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part II: Stability and ageing of bio-oil and its blends with methanol and a pyrolytic aqueous phase, *Biomass and Bioenergy.* 19 (2000) 351–361. [https://doi.org/10.1016/S0961-9534\(00\)00044-1](https://doi.org/10.1016/S0961-9534(00)00044-1).
- [210] A. Oasmaa, J. Korhonen, E. Kuoppala, An Approach for Stability Measurement of Wood-Based Fast Pyrolysis Bio-Oils, *Energy & Fuels.* 25 (2011). <https://doi.org/10.1021/ef2006673>.
- [211] A. Oasmaa, S. Czernik, Fuel Oil Quality of Biomass Pyrolysis Oils State of the Art for the End Users, *Energy & Fuels.* 13 (1999) 914–921. <https://doi.org/10.1021/ef980272b>.
- [212] A.R. Preet M Singh, James R Keiser, Corrosion Susceptibility of Different Alloys in Pyrolysis Oils, Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States), n.d.
- [213] O.D. Mante, F.A. Agblevor, Storage stability of biocrude oils from fast pyrolysis of poultry litter, *Waste Manag.* 32 (2012) 67–76. <https://doi.org/10.1016/j.wasman.2011.09.004>.
- [214] A. Oasmaa, I. Fonts, M.R. Pelaez-Samaniego, M.E. Garcia-Perez, M. Garcia-Perez, Pyrolysis Oil Multiphase Behavior and Phase Stability: A Review, 2016. <https://doi.org/10.1021/acs.energyfuels.6b01287>.
- [215] Z. Guo, S. Wang, X. Wang, Stability mechanism investigation of emulsion fuels from biomass pyrolysis oil and diesel, *Energy.* 66 (2014) 250–255. <https://doi.org/10.1016/j.energy.2014.01.010>.
- [216] A. Alcalá, A.V. Bridgwater, Upgrading fast pyrolysis liquids: Blends of biodiesel and pyrolysis oil, *Fuel.* 109 (2013) 417–426. <https://doi.org/10.1016/j.fuel.2013.02.058>.
- [217] F.A. Agblevor, O. Mante, N. Abdoulmoumine, R. McClung, Production of Stable Biomass Pyrolysis Oils Using Fractional Catalytic Pyrolysis, *Energy & Fuels.* 24 (2010) 4087–4089. <https://doi.org/10.1021/ef1004144>.
- [218] J. Meng, T.I. Smirnova, X. Song, A. Moore, X. Ren, S. Kelley, S. Park, D. Tilotta, Identification of free radicals in pyrolysis oil and their impact on bio-oil stability, *RSC*



- Adv. 4 (2014) 29840–29846. <https://doi.org/10.1039/C4RA02007C>.
- [219] R.N. Hilten, K.C. Das, Comparison of three accelerated aging procedures to assess bio-oil stability, *Fuel*. 89 (2010) 2741–2749. <https://doi.org/10.1016/j.fuel.2010.03.033>.
- [220] A. Chaala, T. Ba, M. Garcia-Perez, C. Roy, Colloidal Properties of Bio-oils Obtained by Vacuum Pyrolysis of Softwood Bark: Aging and Thermal Stability, *Energy & Fuels*. 18 (2004) 1535–1542. <https://doi.org/10.1021/ef030156v>.
- [221] H. Kim, H. Shafaghat, J. Kim, B.S. Kang, J.-K. Jeon, S.-C. Jung, I.-G. Lee, Y.-K. Park, Stabilization of bio-oil over a low cost dolomite catalyst, *Korean J. Chem. Eng.* 35 (2018) 922–925. <https://doi.org/10.1007/s11814-018-0002-3>.
- [222] T. Sundqvist, Y. Solantausta, A. Oasmaa, L. Kokko, V. Paasikallio, Heat Generation during the Aging of Wood-Derived Fast-Pyrolysis Bio-oils, *Energy & Fuels*. 30 (2016) 465–472. <https://doi.org/10.1021/acs.energyfuels.5b02544>.
- [223] E. Oasmaa, A. Leppaemaeki, E. Koponen, P. Levander, J. & Tapola, 98/01078 Physical characterization of biomass-based pyrolysis liquids. Application of standard fuel oil analyses, *Fuel Energy Abstr.* 39 (1998) 97. [https://doi.org/10.1016/S0140-6701\(98\)97220-4](https://doi.org/10.1016/S0140-6701(98)97220-4).
- [224] H. Aubin, C. Roy, STUDY ON THE CORROSIVENESS OP WOOD PYROLYSIS OILS, *Fuel Sci. Technol. Int.* 8 (1990) 77–86. <https://doi.org/10.1080/08843759008915914>.
- [225] H. Darmstadt, M. Garcia-Perez, A. Adnot, A. Chaala, D. Kretschmer, C. Roy, Corrosion of Metals by Bio-Oil Obtained by Vacuum Pyrolysis of Softwood Bark Residues. An X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy Study, *Energy & Fuels*. 18 (2004) 1291–1301. <https://doi.org/10.1021/ef0340920>.
- [226] A. Oasmaa, D.C. Elliott, S. Müller, Quality control in fast pyrolysis bio-oil production and use, *Environ. Prog. Sustain. Energy.* 28 (2009) 404–409. <https://doi.org/10.1002/ep.10382>.
- [227] C. Di Blasi, Influences of physical properties on biomass devolatilization characteristics, *Fuel*. 76 (1997) 957–964. [https://doi.org/10.1016/S0016-2361\(97\)00096-3](https://doi.org/10.1016/S0016-2361(97)00096-3).
- [228] C.A. Koufopoulos, N. Papayannakos, G. Maschio, A. Lucchesi, Modelling of the pyrolysis of biomass particles. Studies on kinetics, thermal and heat transfer effects, *Can. J. Chem. Eng.* 69 (1991) 907–915. <https://doi.org/10.1002/cjce.5450690413>.
- [229] W.C. Park, A. Atreya, H.R. Baum, Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis, *Combust. Flame*. 157 (2010) 481–494. <https://doi.org/10.1016/j.combustflame.2009.10.006>.
- [230] D.E. Dugaard, R.C. Brown, Enthalpy for Pyrolysis for Several Types of Biomass, *Energy & Fuels*. 17 (2003) 934–939. <https://doi.org/10.1021/ef020260x>.
- [231] P. Das, A. Ganesh, P. Wangikar, Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products, *Biomass and Bioenergy*. 27 (2004) 445–457. <https://doi.org/10.1016/j.biombioe.2004.04.002>.
- [232] Z. Tooyserkani, S. Sokhansanj, X. Bi, J. Lim, A. Lau, J. Saddler, L. Kumar, P.S. Lam, S. Melin, Steam treatment of four softwood species and bark to produce torrefied wood, *Appl. Energy*. 103 (2013) 514–521. <https://doi.org/10.1016/j.apenergy.2012.10.016>.
- [233] D. Chiamonti, A. Oasmaa, Y. Solantausta, Power generation using fast pyrolysis liquids from biomass, *Renew. Sustain. Energy Rev.* 11 (2007) 1056–1086. <https://doi.org/10.1016/j.rser.2005.07.008>.
- [234] P.A. Jensen, B. Sander, K. Dam-Johansen, Pretreatment of straw for power production by pyrolysis and char wash, *Biomass and Bioenergy*. 20 (2001) 431–446. [https://doi.org/10.1016/S0961-9534\(01\)00005-8](https://doi.org/10.1016/S0961-9534(01)00005-8).

- [235] A. Oasmaa, K. Sipilä, Y. Solantausta, E. Kuoppala, Quality Improvement of Pyrolysis Liquid: Effect of Light Volatiles on the Stability of Pyrolysis Liquids, *Energy & Fuels*. 19 (2005) 2556–2561. <https://doi.org/10.1021/ef0400924>.
- [236] W. Chaiwat, I. Hasegawa, J. Kori, K. Mae, Examination of Degree of Cross-Linking for Cellulose Precursors Pretreated with Acid/Hot Water at Low Temperature, *Ind. Eng. Chem. Res.* 47 (2008) 5948–5956. <https://doi.org/10.1021/ie800080u>.
- [237] P. Alvira, E. Tomás-Pejó, M. Ballesteros, M.J. Negro, Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review, *Bioresour. Technol.* 101 (2010) 4851–4861. <https://doi.org/10.1016/j.biortech.2009.11.093>.
- [238] M. Phanphanich, S. Mani, Impact of torrefaction on the grindability and fuel characteristics of forest biomass, *Bioresour. Technol.* 102 (2011) 1246–1253. <https://doi.org/10.1016/j.biortech.2010.08.028>.
- [239] A.A. Boateng, C.A. Mullen, Fast pyrolysis of biomass thermally pretreated by torrefaction, *J. Anal. Appl. Pyrolysis.* 100 (2013) 95–102. <https://doi.org/10.1016/j.jaap.2012.12.002>.
- [240] H. Li, X. Liu, R. Legros, X.T. Bi, C.J. Lim, S. Sokhansanj, Torrefaction of sawdust in a fluidized bed reactor, *Bioresour. Technol.* 103 (2012) 453–458. <https://doi.org/10.1016/j.biortech.2011.10.009>.
- [241] M.J.C. van der Stelt, H. Gerhauser, J.H.A. Kiel, K.J. Ptasinski, Biomass upgrading by torrefaction for the production of biofuels: A review, *Biomass and Bioenergy*. (2011). <https://doi.org/10.1016/j.biombioe.2011.06.023>.
- [242] J.S. Tumuluru, S. Sokhansanj, C.T. Wright, Biomass Torrefaction Process Review and Moving Bed Torrefaction System Model Development, Idaho Falls, ID (United States), 2010. <https://doi.org/10.2172/991885>.
- [243] S. Chang, Z. Zhao, A. Zheng, X. Li, X. Wang, Z. Huang, F. He, H. Li, Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor, *Bioresour. Technol.* 138 (2013) 321–328. <https://doi.org/10.1016/j.biortech.2013.03.170>.
- [244] A. Zheng, Z. Zhao, S. Chang, Z. Huang, K. Zhao, G. Wei, F. He, H. Li, Comparison of the effect of wet and dry torrefaction on chemical structure and pyrolysis behavior of corncobs, *Bioresour. Technol.* 176 (2015) 15–22. <https://doi.org/10.1016/j.biortech.2014.10.157>.
- [245] S. Zhang, Q. Dong, L. Zhang, Y. Xiong, X. Liu, S. Zhu, Effects of water washing and torrefaction pretreatments on rice husk pyrolysis by microwave heating, *Bioresour. Technol.* 193 (2015) 442–448. <https://doi.org/10.1016/j.biortech.2015.06.142>.
- [246] É. Le Roux, M. Chaouch, P.N. Diouf, T. Stevanovic, Impact of a pressurized hot water treatment on the quality of bio-oil produced from aspen, *Biomass and Bioenergy*. 81 (2015) 202–209. <https://doi.org/10.1016/j.biombioe.2015.07.005>.
- [247] A. Aho, N. Kumar, K. Eränen, T. Salmi, M. Hupa, D.Y. Murzin, Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure, *Fuel*. 87 (2008) 2493–2501. <https://doi.org/10.1016/j.fuel.2008.02.015>.
- [248] M. Olazar, R. Aguado, J. Bilbao, A. Barona, Pyrolysis of sawdust in a conical spouted-bed reactor with a HZSM-5 catalyst, *AIChE J.* 46 (2000) 1025–1033. <https://doi.org/10.1002/aic.690460514>.
- [249] T.R. Brown, Y. Zhang, G. Hu, R.C. Brown, Techno-economic analysis of biobased chemicals production via integrated catalytic processing, *Biofuels, Bioprod. Biorefining*. 6 (2012) 73–87. <https://doi.org/10.1002/bbb.344>.
- [250] Y. Zhao, T. Pan, Y. Zuo, Q.X. Guo, Y. Fu, Production of aromatic hydrocarbons through

- catalytic pyrolysis of 5-Hydroxymethylfurfural from biomass, *Bioresour. Technol.* 147 (2013) 37. <https://doi.org/10.1016/j.biortech.2013.07.068>.
- [251] W. Cai, N. Kang, M.K. Jang, C. Sun, R. Liu, Z. Luo, Long term storage stability of bio-oil from rice husk fast pyrolysis, *Energy*. 186 (2019) 115882. <https://doi.org/10.1016/j.energy.2019.115882>.
- [252] A. Oasmaa, D. Meier, Norms and standards for fast pyrolysis liquids, *J. Anal. Appl. Pyrolysis*. 73 (2005) 323–334. <https://doi.org/10.1016/j.jaap.2005.03.003>.
- [253] M.W. Nolte, M.W. Liberatore, Real-Time Viscosity Measurements during the Accelerated Aging of Biomass Pyrolysis Oil, *Energy & Fuels*. 25 (2011) 3314–3317. <https://doi.org/10.1021/ef200675t>.
- [254] A. Oasmaa, E. Kuoppala, S. Gust, Y. Solantausta, Fast Pyrolysis of Forestry Residue. 1. Effect of Extractives on Phase Separation of Pyrolysis Liquids, *Energy & Fuels*. 17 (2003) 1–12. <https://doi.org/10.1021/ef020088x>.
- [255] J.P. Diebold, A review of the toxicity of biomass pyrolysis liquids formed at low temperatures, Golden, CO (United States), 1997. <https://doi.org/10.2172/468520>.
- [256] E. Fratini, M. Bonini, A. Oasmaa, Y. Solantausta, J. Teixeira, P. Baglioni, SANS Analysis of the Microstructural Evolution during the Aging of Pyrolysis Oils from Biomass, *Langmuir*. 22 (2006) 306–312. <https://doi.org/10.1021/la051990a>.
- [257] S. Xiu, A. Shahbazi, Bio-oil production and upgrading research: A review, *Renew. Sustain. Energy Rev.* 16 (2012) 4406–4414. <https://doi.org/10.1016/j.rser.2012.04.028>.
- [258] Y. Fu, J. Ye, J. Chang, H. Lou, X. Zheng, Solid fuel production by hydrothermal carbonization of water-like phase of bio-oil, *Fuel*. 180 (2016) 591–596. <https://doi.org/10.1016/j.fuel.2016.04.089>.
- [259] F. Abnisa, A. Arami-Niya, W.M.A.W. Daud, J.N. Sahu, Characterization of Bio-oil and Bio-char from Pyrolysis of Palm Oil Wastes, *BioEnergy Res.* 6 (2013) 830–840. <https://doi.org/10.1007/s12155-013-9313-8>.
- [260] D. Mourant, C. Lievens, R. Gunawan, Y. Wang, X. Hu, L. Wu, S.S.A. Syed-Hassan, C.-Z. Li, Effects of temperature on the yields and properties of bio-oil from the fast pyrolysis of mallee bark, *Fuel*. 108 (2013) 400–408. <https://doi.org/10.1016/j.fuel.2012.12.018>.
- [261] D.C. Elliott, A. Oasmaa, F. Preto, D. Meier, A. V. Bridgwater, Results of the IEA Round Robin on Viscosity and Stability of Fast Pyrolysis Bio-oils, *Energy & Fuels*. 26 (2012) 3769–3776. <https://doi.org/10.1021/ef300384t>.
- [262] S. Czernik, D.K. Johnson, S. Black, Stability of wood fast pyrolysis oil, *Biomass and Bioenergy*. 7 (1994) 187–192. [https://doi.org/10.1016/0961-9534\(94\)00058-2](https://doi.org/10.1016/0961-9534(94)00058-2).
- [263] R.N. Hilten, K.C. Das, Comparison of three accelerated aging procedures to assess bio-oil stability, *Fuel*. 89 (2010) 2741–2749. <https://doi.org/10.1016/j.fuel.2010.03.033>.
- [264] E. Alsbou, B. Helleur, Accelerated Aging of Bio-oil from Fast Pyrolysis of Hardwood, *Energy & Fuels*. 28 (2014) 3224–3235. <https://doi.org/10.1021/ef500399n>.
- [265] J. V. Ortega, A.M. Renehan, M.W. Liberatore, A.M. Herring, Physical and chemical characteristics of aging pyrolysis oils produced from hardwood and softwood feedstocks, *J. Anal. Appl. Pyrolysis*. 91 (2011) 190–198. <https://doi.org/10.1016/j.jaap.2011.02.007>.
- [266] X. Jiang, Z. Zhong, N. Ellis, Q. Wang, Aging and Thermal Stability of the Mixed Product of the Ether-Soluble Fraction of Bio-Oil and Bio-Diesel, *Chem. Eng. Technol.* 34 (2011) 727–736. <https://doi.org/10.1002/ceat.201000441>.
- [267] A. Oasmaa, E. Kuoppala, Fast Pyrolysis of Forestry Residue. 3. Storage Stability of Liquid Fuel, *Energy & Fuels*. 17 (2003) 1075–1084. <https://doi.org/10.1021/ef030011o>.
- [268] L. Leng, H. Li, X. Yuan, W. Zhou, H. Huang, Bio-oil upgrading by emulsification/microemulsification: A review, *Energy [1] Jena U, Das KC. Comp. Eval.*

- Thermochem. Liq. Pyrolysis Bio-Oil Prod. from Microalgae. *Energy Fuel* 2011;25 5472e82. <https://doi.org/10.1021/ef201373m>. [2] Huang H, Yuan X. *Recent Prog. Direct Liq.* 161 (2018) 214–232. <https://doi.org/10.1016/j.energy.2018.07.117>.
- [269] A. Chaala, T. Ba, M. Garcia-Perez, C. Roy, Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark: Aging and thermal stability, *Energy and Fuels*. 18 (2004) 1535–1542. <https://doi.org/10.1021/ef030156v>.
- [270] J. Meng, A. Moore, D. Tilotta, S. Kelley, S. Park, Toward Understanding of Bio-Oil Aging: Accelerated Aging of Bio-Oil Fractions, *ACS Sustain. Chem. Eng.* 2 (2014) 2011–2018. <https://doi.org/10.1021/sc500223e>.
- [271] T. Ba, A. Chaala, M. Garcia-Perez, C. Roy, Colloidal Properties of Bio-Oils Obtained by Vacuum Pyrolysis of Softwood Bark. *Storage Stability, Energy & Fuels*. 18 (2004) 188–201. <https://doi.org/10.1021/ef0301250>.
- [272] R.M. Connatser, S.A. Lewis, J.R. Keiser, J.-S. Choi, Measuring bio-oil upgrade intermediates and corrosive species with polarity-matched analytical approaches, *Biomass and Bioenergy*. 70 (2014) 557–563. <https://doi.org/10.1016/j.biombioe.2014.09.003>.
- [273] J.R. Keiser, S.A. Lewis, Degradation of structural alloys in biomass-derived pyrolysis oil Seed oil validation View project Materials Degradation in Biomass-derived Oils View project, n.d. <https://www.researchgate.net/publication/285678259> (accessed March 15, 2020).
- [274] Q. Lu, J. Zhang, X. Zhu, Corrosion properties of bio-oil and its emulsions with diesel, *Chinese Sci. Bull.* 53 (2008) 3726–3734. <https://doi.org/10.1007/s11434-008-0499-7>.
- [275] J. Keiser, M. Howell, S. Lewis, R.C.-C. 2012, undefined 2012, Corrosion studies of raw and treated biomass-derived pyrolysis oils, *Onepetro.Org.* (n.d.). <https://www.onepetro.org/conference-paper/NACE-2012-1645> (accessed March 15, 2020).
- [276] B. Fekhar, L. Gombor, N. Miskolczi, Pyrolysis of chlorine contaminated municipal plastic waste: In-situ upgrading of pyrolysis oils by Ni/ZSM-5, Ni/SAPO-11, red mud and Ca(OH)<sub>2</sub> containing catalysts, *J. Energy Inst.* (2018). <https://doi.org/10.1016/j.joei.2018.10.007>.
- [277] B. Fekhar, V. Zsinka, N. Miskolczi, Value added hydrocarbons obtained by pyrolysis of contaminated waste plastics in horizontal tubular reactor: In situ upgrading of the products by chlorine capture, *J. Clean. Prod.* 241 (2019) 118166. <https://doi.org/10.1016/j.jclepro.2019.118166>.
- [278] D. Yao, H. Yang, H. Chen, P.T. Williams, Co-precipitation, impregnation and so-gel preparation of Ni catalysts for pyrolysis-catalytic steam reforming of waste plastics, *Appl. Catal. B Environ.* (2018). <https://doi.org/10.1016/j.apcatb.2018.07.075>.
- [279] Y. Yu, Y.W. Chua, H. Wu, Characterization of Pyrolytic Sugars in Bio-Oil Produced from Biomass Fast Pyrolysis, *Energy & Fuels*. 30 (2016) 4145–4149. <https://doi.org/10.1021/acs.energyfuels.6b00464>.
- [280] Z. Czégény, E. Jakab, J. Bozi, M. Blazsó, Pyrolysis of wood–PVC mixtures. Formation of chloromethane from lignocellulosic materials in the presence of PVC, *J. Anal. Appl. Pyrolysis*. 113 (2015) 123–132. <https://doi.org/10.1016/j.jaap.2014.11.016>.
- [281] S.D. Anuar Sharuddin, F. Abnisa, W.M.A. Wan Daud, M.K. Aroua, A review on pyrolysis of plastic wastes, *Energy Convers. Manag.* 115 (2016) 308–326. <https://doi.org/10.1016/j.enconman.2016.02.037>.
- [282] C. Zhao, E. Jiang, A. Chen, Volatile production from pyrolysis of cellulose, hemicellulose and lignin, *J. Energy Inst.* 90 (2017) 902–913. <https://doi.org/10.1016/j.joei.2016.08.004>.
- [283] S.M. Grimes, H. Lateef, A.J. Jafari, L. Mehta, Studies of the effects of copper, copper(II) oxide and copper(II) chloride on the thermal degradation of poly(vinyl chloride), *Polym.*

- [284] J. Yanik, M.A. Uddin, K. Ikeuchi, Y. Sakata, The catalytic effect of Red Mud on the degradation of poly (vinyl chloride) containing polymer mixture into fuel oil, *Polym. Degrad. Stab.* 73 (2001) 335–346. [https://doi.org/10.1016/S0141-3910\(01\)00095-7](https://doi.org/10.1016/S0141-3910(01)00095-7).
- [285] T. Karayildirim, J. Yanik, M. Yuksel, M. Saglam, C. Vasile, H. Bockhorn, The effect of some fillers on PVC degradation, *J. Anal. Appl. Pyrolysis.* 75 (2006) 112–119. <https://doi.org/10.1016/j.jaap.2005.04.012>.
- [286] A. Adrados, I. de Marco, B.M. Caballero, A. López, M.F. Laresgoiti, A. Torres, Pyrolysis of plastic packaging waste: A comparison of plastic residuals from material recovery facilities with simulated plastic waste, *Waste Manag.* 32 (2012) 826–832. <https://doi.org/10.1016/j.wasman.2011.06.016>.
- [287] O.H. Ahmed, M. Altarawneh, Z.-T. Jiang, M. Al-Harashseh, B.Z. Dlugogorski, Reactions of products from thermal degradation of PVC with nanoclusters of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite), *Chem. Eng. J.* 323 (2017) 396–405. <https://doi.org/10.1016/j.cej.2017.04.047>.
- [288] B. Fekhar, V. Zsinka, N. Miskolczi. 2020. Thermo-catalytic co-pyrolysis of waste plastic and paper in batch and tubular reactors for in-situ product improvement, *Journal of Environmental Management* 269, (2020) 110741. <https://doi.org/10.1016/j.jenvman.2020.110741>
- [289] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor, *Chem. Eng. J.* 173 (2011) 62–71. <https://doi.org/10.1016/j.cej.2011.07.037>.
- [290] J. Wu, T. Chen, X. Luo, D. Han, Z. Wang, J. Wu, TG/FTIR analysis on co-pyrolysis behavior of PE, PVC and PS, *Waste Manag.* 34 (2014) 676–682. <https://doi.org/10.1016/j.wasman.2013.12.005>.
- [291] G. Özsın, A.E. Pütün, A comparative study on co-pyrolysis of lignocellulosic biomass with polyethylene terephthalate, polystyrene, and polyvinyl chloride: Synergistic effects and product characteristics, *J. Clean. Prod.* 205 (2018) 1127–1138. <https://doi.org/10.1016/j.jclepro.2018.09.134>.
- [292] G. Özsın, A.E. Pütün, TGA/MS/FT-IR study for kinetic evaluation and evolved gas analysis of a biomass/PVC co-pyrolysis process, *Energy Convers. Manag.* 182 (2019) 143–153. <https://doi.org/10.1016/j.enconman.2018.12.060>.
- [293] F. Bahmed, N. Miskolczi, V. Zsinka, Fuels by chemical recycling of waste plastic and biomass mixture and utilization of the products, *Chem. Eng. Trans.* 76 (2019) 1447–1452. <https://doi.org/10.3303/CET1976242>.