HYDROGEN PRODUCTION BY WASTE PLASTICS PYROLYSIS-GASIFICATION USING TRANSITION METAL-CONTAINING CATALYSTS

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„HYDROGEN PRODUCTION BY WASTE PLASTICS PYROLYSIS-GASIFICATION USING TRANSITION METAL-CONTAINING CATALYSTS”

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ABSTRACT

In this work, real waste plastic mixture of high density polyethylene, low density polyethylene, polypropylene and poly ethylene terphthalte were used as raw materials for the production of hydrogen rich syngas using pyrolysis and gasification processes. The expirements were took place in a horizontal tubular reactor (one and two stages) in the presence of different catalyst type and various reaction temperature. The influence of process parameters such as reactor temperature (500 – 900 °C) and atmosphere (N_2, O_2 and CO_2) on the product yields were studied. For the catalytic process, different catalyst supports (ZSM-5, y-zeolite, β-zeolite and natural zeolite) with different active metals (Ni, Co, Fe V and Zn) were investigated. Among the various catalysts, Ni/ZSM-5 showed advanced property in gas yield increasing at high temperature. The Ni/ZSM-5 catalyst was further modified with five second metals of Ca, Ce, La, Mg and Mn. These metals were used as promoters at different concentratios. The modified catalysts can enhanced the reaction rate of the pyrolysis process and resulting in high syngas in the product yields. Results showed that highest hydrogen and syngas yield were observed using Ce and La coverd catalysts. Also, higher concentration of second metals can block the catalyst pore channels due to the more coke formation. The results also demonstrated that higher reaction temperature resulted in more syngas product and the maximum yield was obtained at 850 °C. Moreover, atmosphere has great influence on the gasification process as it can effect the hydrogen yield and carbon deposition on the catalyst surface. However, owing to the gasification reaction, pyrolysis oil yield was decreased wih rising the temperature.

Keywords: hydrogen; syngas; waste plastic; transition metal loaded catalysts; pyrolysis-gasification

الملخص

في هذا العمل ، تم استخدام خليط من مخلفات البلاستيك الحقيقي المكون من البولي إيثيلين عالي الكثافة والبولي إيثيلين واطئ الكثافة والبولي بروبيلين والبولي إيثيلين تيرفثاليت كمواد اولية لإنتاج غاز التخليق الغني بالهيدروجين باستخدام عمليات التحلل الحراري والتغويز. تمت التجارب في مفاعل أنبوبي أفقي (مرحلة واحدة و مرحلتان) بوجود محفزات مختلفة وعند درجات حرارة تفاعل مختلفة. تمت دراسة تأثير عدة عوامل على حاصل الأنتاج مثل درجة حرارة المفاعل (500-900 درجة مئوية) وبيئة التفاعل (نتروجين و الأوكسجين و ثاني اوكسيد الكاربون). للعملية التحفيزية ، تم فحص عدة محفزات منها (ZSM-5، y-zeolite، β-zeolite والزيولايت الطبيعي) مع معادن نشطة مختلفة مثل (Ni، Co، Fe V، Zn). من بين المحفزات المختلفة ، أظهر Ni / ZSM-5 خاصية متقدمة في زيادة إنتاج الغاز عند درجات الحرارة العالية. تم تطوير المحفز Ni / ZSM-5 بأضافة خمس معادن ثانوية مكونه من Ca و Ce و La و Mg و Mn. تم استخدام هذه المعادن كمعززات بتراكيز مختلفة. يمكن للمحفزات المعدلة أن ترفع من معدل تفاعل عملية الانحلال الحراري وتؤدي إلى إنتاج غاز تخليقي مرتفع في الناتج النهائي. أظهرت النتائج أن أعلى إنتاجية للهيدروجين وغاز التخليق لوحظت باستخدام محفزات Ce وLa. أيضًا ، يمكن أن يؤدي التركيز العالي للمعادن الثانية إلى سد قنوات مسام المحفز بسبب زيادة تكوين فحم الكوك. أظهرت النتائج أيضًا أن درجة حرارة التفاعل الأعلى أدت إلى إنتاج المزيد من غاز التخليق وتم الحصول على أعلى إنتاج عند 850 درجة مئوية. علاوة على ذلك ، فإن بيئة التفاعل لها تأثير كبيرعلى عملية التحويل الغازي لأنها يمكن أن تؤثر على محصول الهيدروجين وترسب الكربون على سطح المحفز. ومع ذلك ، بسبب تفاعل التغويز ، انخفض إنتاج زيت الانحلال الحراري مع ارتفاع درجة الحرارة للمفاعل.

الكلمات الدالة: الهيدروجين؛ الغاز التخليقي؛ مخلفات البلاستيك ؛ محفزات معدنية انتقالية ؛ التغويز- التحلل الحراري

ABBREVIATION

BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BTU	British Thermal Unit
°C	Degree celsius
CNTs	Carbon Nanotubs
DTG	Derivative Thermogravimetric Analysis
Ea	Activation Energy
FID	Flame Ionization Detector
EF	Entrained Flow gasifier
FID	Flame Ionization Detector
FTIR	Fourier-Transfourm Infrrared Spectroscopy
GC	Gas Chromatography
HDPE	High Density Polyethylene
h	Hour
LDPE	Low Density Polyethylene
Min	Minute
mg	Milligram
MSW	Municipal Solid Waste
N_2	Nitrogen
PET	Poly Ethylene Terephthalate
PP	Ploypropylene
PS	Poly Styrene
PVC	Polyvinyl Chloride
SEM	Scanning Electron Microscopy
Si/Al	Silica/Alumina
TCD	Thermal Conductivity Detector
TEM	Transmison Electron Microscopy
TGA	Thermogravimetric Analysis
TPO	Temperature Programmed Oxidation

Veszprém, Hungary, 28. 09. 2021

STATEMENT

Undersigned Mohammed Al-asadi hereby declares that the “*Hydrogen production by waste plastics pyrolysis-gasification using transition metal-containing catalysts*” 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 dissertations 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.

Mohammed Abdulraheem Saeed Al-asadi

To Israa,

my amazing wife,

whose sacrificial care for me and our children

made it possible for me to complete this work,

and to our children,

Sarah and Adam

who are indeed a treasure from the God

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

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I dedicate this work to my dear parents, brothers and sisters for their endless support and encouragement throughout my studies. Moreover, all my friends who have supported me during these four years.

Mohammed Abdulraheem Saeed Al-asadi

INTRODUCTION

Plastic plays a significant role in our daily life due to the vast used for different application sectors such as packaging, electronic, health care, automotive, etc [1]. Fast growing of world population, low production cost and long service life are the main factors that led to increasing of plastic consumption. The accumulation of global plastic waste increased in dramatic way as a result of the continuous plastic demand. Plastics are materials with hydrocabons base as its manufactured by petroleum products [2]. Hence, from energy point of view and due to the high energy demand, the hidden energy from waste plastic can be recoverd by the application of appropriate recycling method. Therefore, waste plastic recycling not only reduced the plastic disposal, but can minimize the dependence of fossile fuel as a source of energy.

Moreover, the proper waste recycling can meet the world energy demand and prevent the environment from the contamination. Pyrolysis process is one of the most attractive way for energy and feedstock production from waste materials (plastic and biomass). The process can carried out in the presence of catalyst or thermally without catalyst. Catalyst can increase the conversion rate of waste polymers and minimize the energy required for the decomposition reaction.

In order to obtaine the optimum conditions for hydrogen/syngas production, many catalysts have been investigated for pyrolysis of waste plastics. Other process parameters such as temperature, carrier gas and residence time are also influnced the syngas and hydrogen yield. The amount and quality of the produced gas are important from economic point of view.

The main goal of the current study is to investigate the influnce of proccess parameters (temperature, type of carrier gas), catalyst type and plastic/catalyst ratio on the products yield from real waste plastic mixture. The effect of second metal promoters on the catalyst performane was also studied. Furthermore, the pathway for the decomposition reaction was also investigated by studying the kinetic parameters to obtain more information about pyrolysis process. The current study can provide more understanding about the role and effect of second promoter in the degradation of waste plastics.

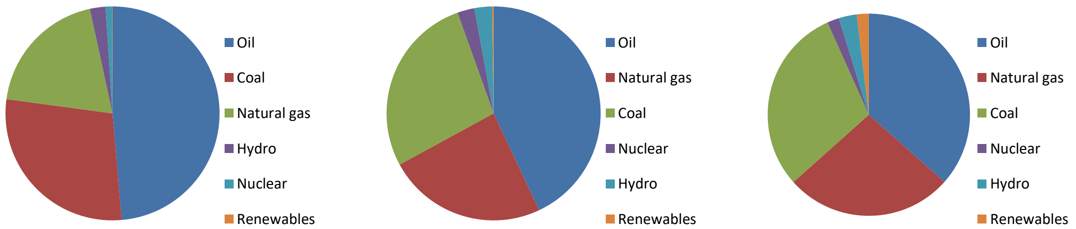
1. LITERATURE SURVEY

1.1. Energy dependence

The world energy demand is still increasing. Oil, coal and gas are the main source of fuel that supply the energy and electricity. During the fossil fuel burning, the carbon reacts with the oxygen in the air and form carbon dioxide. Carbon monoxide, nitrogen oxides and sulfur oxides are toxic gases that release to the atmosphere during the combustion process of fossil fuels and causing air pollution [3]. Many studies have been established on the negative effects of fossil fuel as energy source [4, 5].

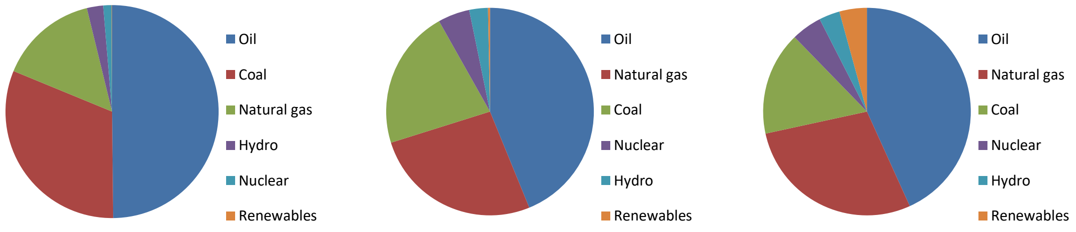
The global warming is one of the most challenges that associated with energy supply and utilization. Moreover, health and economic problems have been addressed as a consequence of air pollution. Hence, the quality of life even in modern countries can be affected by the environmental problems of fossil fuel based energy production [6-8].

The depletion of fossil fuel availability is another drawback in its utilization for the future energy. European countries have implemented a new polices in order to reducing the fossil fuel consumption. In spite of the new strategies, most of European countries still dependent on fossil fuels as the main source for energy, however, forecasts predict significant increase in the application of renewable energy sources **(Figures 1.1 and 1.2)** [9, 10].



World (1980) World (2000) World (2020)

Figure 1.1
The main energy sources in worldwide (1980, 2000, 2020) [11]



EU (1980) EU (2000) EU (2020)

Figure 1.2
The main energy sources in the EU (1980, 2000, 2020) [11]

One of the options to reduce the fossil fuel dependene is the waste utilization for energy purposes. By this way not only the energy dependence should be reduced, but also the amount of wastes could be minimized. Therefore many of the directives and laws try to accelerate the utilization of wastes for energy purpose.

1.2. Problems of waste plastic

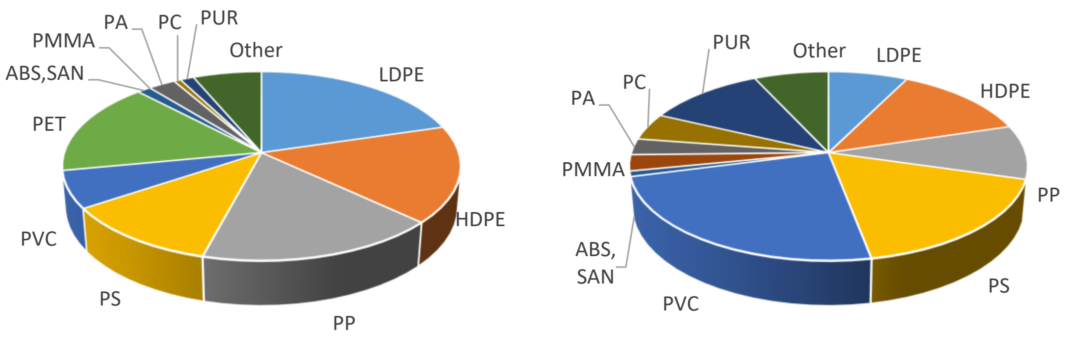
Many types of wastes are everywhere from biomass through plastics to toxic wastes. There are many possibilities for waste classification: e.g. industrial or municipal wastes, hazardous or non-hazardous, solid, liquid or gas phase wastes, etc. The highly demand for plastic led to dramatic increasing of the global production from 1.5 million tons per year in the 1950 to 368 million tons per year in 2019 [12]. Many reasons are behind the widespread of plastic materials such as, low production cost, versatility, durability, long service life and corrosion resistance [13].

Waste plastics are unique comparing to other wastes. The most problem with the plastics, that due to their advanced chemically resistance, they will remain in the environment for a very long time to completely degrade [14]. That is why the waste plastics are accummuated and can poisoning the environment. The ingestion of theses wastes by living organisms caused a serious physical problems [15]. In addition to the physical effects of waste plastics, it has also chemical impacts on the living organisms [16]. Chemical pollutants can be found in the form of organo chlorine pesticides, poly chlorinated biphenyls and poly cyclic aromatic hydrocarbons [17, 18]. However, these compounds are toxic and the toxicity level of these chemicals are depends on the amount of the ingested plastic. Waste plastic not only poses a threat to the aquatic organisms but also causes human health problems, soil and water pollution [19]. In many countries, the management policies are insufficient which contributed in more waste plastic accumulation. On the long term basis, the leaching of some chemicals and additives from waste plastic lead to the contamination of soil and groundwater [20, 21].

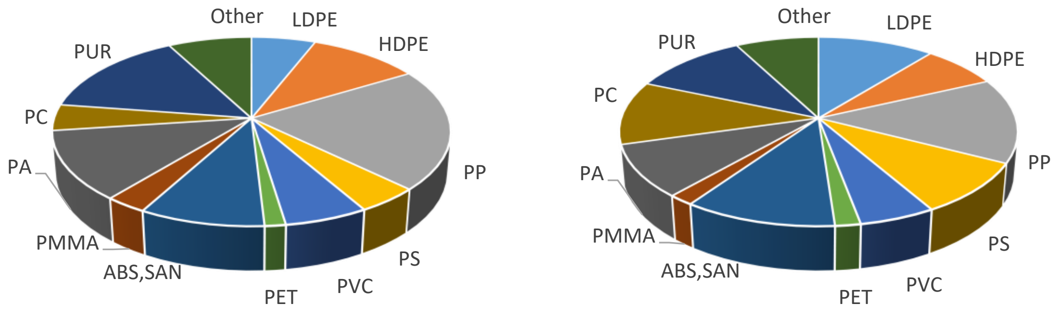
On the other hand waste plastics have many advantageous properties for their utilization. Most of the plastics contains only carbon and hydrogen (e.g. HDPE, LDPE, PP, PS), or carbon, hydrogen and oxygen (e.g. PET, PC), or carbon, hydrogen, oxygen and nitrogen (e.g. PA, PUR), or carbon, hydrogen and chlorine (e.g. PVC). Due to the chemical composition of waste plastics, they have high energy content, which means that considerable energy could be saved by resonable recycling. Thus, recycling of waste plastic is a matter of great importance to conserve energy and solve the rise in the prices of virgin plastics. Currently, extensive studies and researches are focusing on the effects of waste plastics on the environment. HDPE, LDPE, PET, PS and PVC are characterized as the most commonly used plastics [22].

1.3. Main constituents in plastic wastes

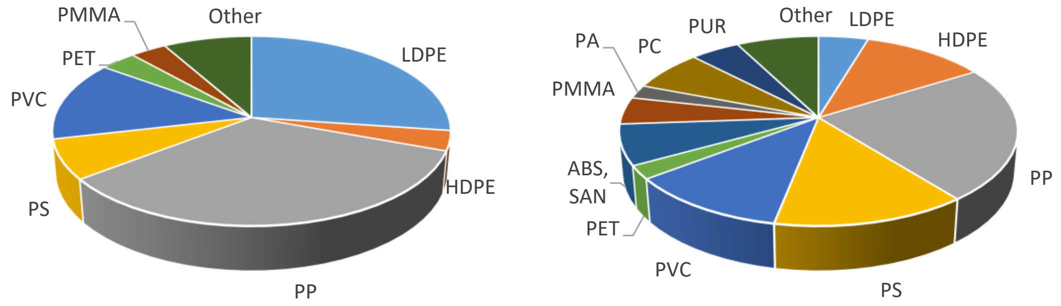
The composition of plastic waste is affected by many factors. There are significant differences in the amount and composition of plastic waste among countries and different types of settlements. Fact, that the developed countries and cities use significantly more plastics than developing countries or village. Therefore, the plastic content of waste from developed countries or cities will also be much higher. In addition, in the case of cities, waste (and plastic waste) is more concentrated due to the larger population per area unit. In addition, in the composition of the plastic content of household waste, commodity plastics are dominant, while plastic waste from industrial sources contains a significant amount of engineering plastic. The average composition of plastics in different sectors is shown in **Figure 1.3**. Plastic wastes from agricultural and packaging sectors are reach in polyethylene and polypropylene. The municipal plastic wastes contain significant amount of polyethylene, polypropylene and polyethylene-terephtalate, because the dominant amount of the used PET bottles are accumulated in the household wastes.



Packaging Building and construction



Automotive Electric and electronic



Agriculture Household, leisure and sports

Figure 1.3
The average composition of plastic wastes by sectors [12]

1.4. Methods for waste utilization

Increasing the amount of waste plastic is a normal consequence of the high consumption. This led to a continuous growing of the annual waste due to the continuous utilization (demand) of plastic materials. Many efforts have been implemented in order to decrease the waste plastic generation and meet the concerns regarding our environment. The environmental problems associated with plastic waste including air, water and soil pollution could be mitigate by the recycling of these wastes [23]. The diversion of plastic into landfill can be avoided by the application of recycling technologies [24]. From the above mentioned reasons, utilization of waste plastic through recycling process is the best option in terms of waste management and energy saving. Additionally, the strategy of waste recycling participates in the minimizing of waste quantities requiring disposal. The **Table 1.1** summarizes the main aspects of the commonly used waste utilizations. Regarding the landfill, the leaching of toxic chemicals to the ground water, polluting of soil, consume a lot of space and the negative effects on human health are the most problems. The incineration releases of many dangerous compounds such as toxic gases to the atmosphere and toxic chemicals are transported into the ground water during the rainfall which affects the aquatic system. Contrary, recycling of plastic wastes had less environmental concerns compared to landfilling and incineration. Henceforward, they are more environmental friendly, can produce valuable products and conserve the limited conventional resources.

Table 1.1
The commonly used waste utilizations [23, 25, 26]

Methods	Adavantage	Disadvantage
Landfilling	No treatment step such as seperation or cleaning steps. Low cost.	Leaching of toxic chemicals to the ground water, polluting of soil, consume a lot of space. Negative effects on human health
Incineration	Recover the energy from the wastes. Reduce the landfilling.	Release of many dangerous compounds such as toxic gases to the atmosphere. Some toxic chemicals are transported into the ground water during the rainfall which affects the aquatic system.
Mechanical recycling	Less environmental concerns compared to landfilling and incineration. Low operation cost.	The numbers of recycling are limited. The physical properties of the product may differ due to the exposure to heat, light, oxidation, etc.
Chemical recycling	More environmental friendly. Produce valuable products. Conserve the limited conventional resources.	High operation cost.
Solvo/hydrotreatment	Feedstock with a certain wet content can feed directly without drying step.	High operation cost.

1.5. Hydrogen/syngas based solution

The demand for clean fuels has been increased due to the fossil fuel problems (long term availability vs. price), its environmental issues and growing of world population. Product pricing is another challenge that affecting the cost and consumption of fossil fuels due to the new energy policies [27]. The substitution of the conventional energy system is required in order to eliminate the negative effects of fossil fuels. Hydrogen and syngas (mixture of H_2 and CO) are the most promising to switching the fossil fuels for the future energy [28].

Hydrogen has gained the attention due to its clean burning qualities as the water is produced from its combustion. The versatility of syngas utilization is another key factor for the replacement of fossil fuel **(Figure 1.4)**. In the chemical industry, syngas is a promising feedstock for the manufacturing of different valuable chemicals such as, hydrogen, ammonia, ethanol, methanol and liquid hydrocarbons. A thermochemical and microbial processes are used for the conversion of syngas into a useful compounds [29].

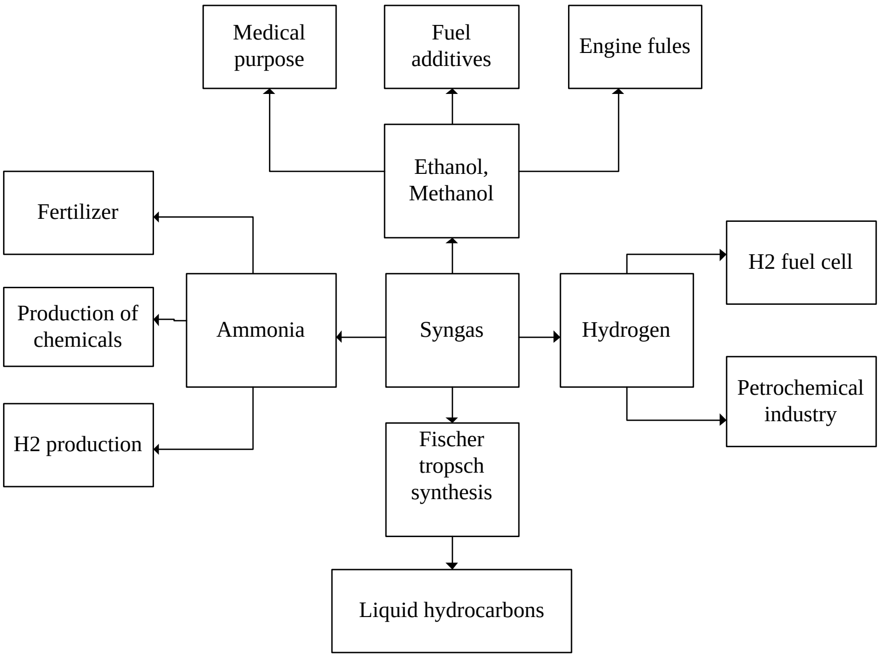


Figure 1.4
The possible utilizaitons of syngas

In addition, syngas is a noble option to obtain sustainable development as it should be produced from renewable resources. Hence, the dependence on fossil fuels for energy system could be eliminated as these fuel considered as non-renewable. Furthermore, the emiisions from fossil fuel and their negative impact on the environment could be also reduced. Hydrogen and syngas can be used for various application such as fuel cell, fuel for internal engine combustion and fuel for steam turbine to produce heat and electricity [30]. Currently, the availability of feedstock is the most challenge that facing refineries and petrochemical industry. Syngas can be used as a feedstock for petrochemical processes. In industrial applications, syngas used to supply the hydrogen to the refineries and fertilizers. Also, its used to produce liquid fuels, carbon monoxide, methanol, etc. [31].

Hydrogen from syngas is widely used for the production of ammonia and methanol, while in refineries, hydrogen is utilized for the hydro treating [32, 33]. Moreover, a certain amount of the produced hydrogen used for the hydrogenation reactions and manufacturing of aniline and other chemicals. Hence, hydrogen plays a significant role in the chemical industry [34]. In addition, ethanol from syngas is considered as an efficient fuel to replace the convential fuels and lowering the effects of greenhouse gases. Henstra et al, 2007 used microbiology process for ethanol production from syngas [35]. Similary, Younesi et al, 2005 carried out the microbial process for ethanol generation [36]. Beside the microbial process, thermochemical processes of syngas are used for the manufacturing of ethanol through the hydrogenation of carbon monoxide and carbon dioxide. This method is more desirable and efficient in comparison to microbial process as the amount of ethanol produced is larger. Syngas is also an efficient fuel that can be utilized for the internal combustion engines to generate heat and electricity.

1.5.1. Thermal process for hydrogen/syngas production

The scale of operation is one of the significant factor that contributes in the selection of syngas production method. Most of hydrogen production methods are based on the natural gas such as methane. Natural gas and methane represent the most feedstock for the world hydrogen production.

1.5.1.1 Steam reforming of methane

Syngas production through reacting methane with steam is widely used. It is involves methane reforming in the presence of catalyst to produce hydrogen and carbon monoxide **(Figure 1.5)**.

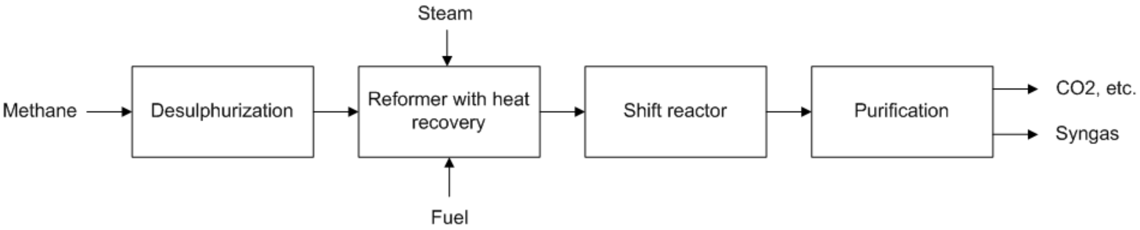


Figure 1.5
Schematic diagram for methane steam reforming

In this process, the reaction is endothermic and carried out at elevated temperature. Thus, indirect heating is needed to provide the required heat to the process. High reaction temperature, high steam excess and low pressure are the best conditions to optimize the hydrogen yield in this process [37]. The abundance of methane and water feedstock is one of the features for this process. Steam reforming has a good process kinetics and can be operates at low pressure. A purification system is applied for pretreatment of feedstock to remove sulfur and other impurities [37]. However, the application of steam reforming method is based on the availability of natural gas in a huge quantity. Catalysts have been used in the catalytic steam reforming in order to obtain the maximum yield of syngas. Matsumura and Nakamori conducted the steam reforming of methane for hydrogen production over various catalyst supports of zirconia, silica and y-alumina. The influence of different support on the nickel catalyst was investigated. They found that zirconia with nickel showed higher efficiency in the steam reforming compared to other catalyst supports [38].

A number of nickel based catalysts were used by Nieva et al for the methane steam reforming at temperature of 500 and 600°C. Among the different metal supports, catalyst of Ni-Zn-Al presented the best activity in the catalytic steam reforming of methane [39]. Li et al studied the performance of different catalysts on the syngas production from methane reforming. The authors observed that the catalyst performance is affected by the type of preparation method. The performance of nickel based catalyst for the reforming of methane would be enhance by the addition of small amount of noble metals [40].

1.5.1.2 Partial oxidation of methane

Partial oxidation of methane is another efficient method for the syngas production. The required amount of heated steam can be avoided by the application of this method as its exothermic process **(Figure 1.6)** [41]. Controlling the selectivity of the reaction is one of the challenging that facing this process. According to the literatures, two reaction mechanisms are involved in this process which are; direct mechanism and combustion reforming mechanism. In the direct mechanism, the methane reacted with oxygen to produce hydrogen and carbon monoxide, while in the combustion-reforming, the water and CO_2 are produced from the reaction of methane and oxygen then steam and dry reforming reaction of the excess CH_4 produce the syngas [37] *(1.1 and 1.2).*

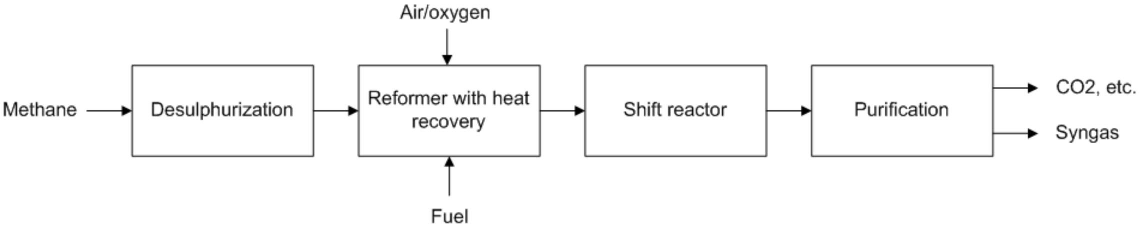


Figure 1.6
Schematic diagram for partial oxidation

Similar to methane steam reforming, partial oxidation is favoured at high temperature. In contrast, the reaction for partial oxidation is more efficient and faster compared to steam reforming as the reaction is exothermic. Catalyst also plays a vital role in the production of syngas from the partial oxidation of methane. Moreover, the syngas yield from catalytic partial oxidation has 2:1 H_2/CO ratio which can be used directly for the production of methanol and Fischer-Tropsch synthesis [37].

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \tag{1.1}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{1.2}$$

Tianli et al have done the partial oxidation of methane over Ni/CeO_2 catalyst with different nickel content. Similar results were reported for the various catalysts towards the syngas yield at high temperature. However, catalyst with 5% nickel content had the lowest amount of carbon deposition [42].

In another work, Patric et al carried out the partial oxidation process of methane using various metal catalysts (Ni, Pt, Pd, Rh, Ir and Ru). They observed that syngas yield was increased with increasing the temperature [43]. Asencios et al combained the partial oxidation with dry reforming of methane over NiO-MgO-ZrO_2 with different nickel content. Catalyst with nickel content of 20 wt% was the best in terms of catalyst performance in comparison to other used catalysts. Their results demonstrated a high conversion rate due to the combination of the two process [44]. Moreover, Badmaev et al performed the partial oxidation process for syngas production over catalyst of Rh/Ce/ZrO_2 and composite Rh/Ce/ZrO_2/Al_2O_3/FeCrAl at temperature range of 300 to 700°C. The authors reported that composite catalyst showed high activity in terms of feedstock conversion. Also, the maximum yield of syngas products was obtained at elevated temperature [45].

1.5.1.3 Waste gasification technology

Gasification is a method for syngas production based on the thermo-chemical conversion of different feedstock such as biomass, waste plastic, coal and petroleum based feedstock. Gasification has gained the attention recently due to its ability for syngas production and feedstock flexibility **(Figure 1.7)**.

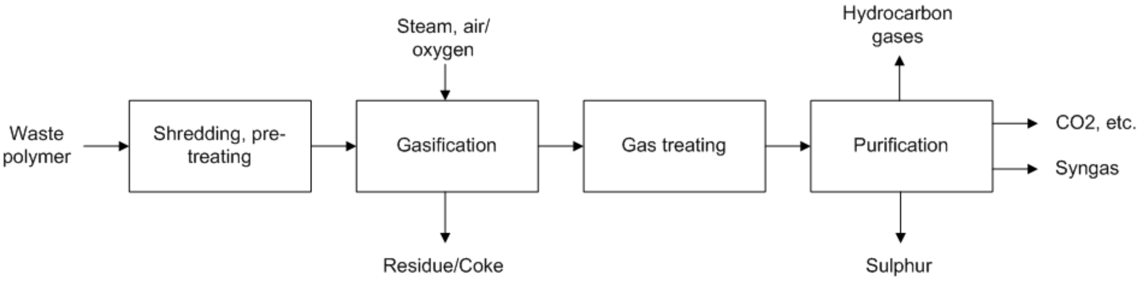


Figure 1.7
Schematic diagram for gasification process

Generally, the gasification process is carried out at temperature range of 500-900°C in the presence of steam, air, oxygen, carbon-dioxide which are called gasifying agents. Gasification are differ based on some categories such as heat supplier, agent type, temperature, etc [46]. The calorific value of the product gas may decline when the air introduced to the gasifier due to the presence of air which dilutes the gas yield. However, there are different types of gasifiers such as entrained flow gasifier and bubbling fluidized bed gasifier. In principle, the feedstock for entrained flow gasifier should be treated and must be in small size due to the short residence time. Therefore, some extra cost are needed in this process for the pre-treatment step [47].

In terms of large scale production, the entrained flow gasifier is appropriate for the gasification of coal and petroleum based materials. Hence, gasification technology is a suitable for industrial and commercial applications [48]. Muhammad Irfan perform the gasification technology for the production of hydrogen rich syngas from municipal solid waste using a fixed bed reactor. Waste marble powder with different ratios was used as a catalyst for this process at various temperature and steam rate. The authors observed a significant effect of steam, temperature and catalyst on the syngas yield from the gasification of municipal solid waste [49].

1.6. Hydrogen/syngas by pyrolysis-reforming of waste plastic

The potential for waste plastic conversion into valuable energy has gained more interest by many studies in order to meet the increasing demand for energy. Due to the hydrocarbon base and high calorific value of waste plastic materials, therefore, valuable energy can be obtained by the conversion of these wastes. The main conclusions of recently published researches focussing to the syngas production are summarized in **Table 1.2**.

Table 1.2

The main conditions and conclusions for waste based syngas production

Raw materials	Reactors	Parameters	Main results	Reference
HDPE, pine sawdust	Two- stages fixed bed reactor	550-750 °C, N_2, PS/HDPE ratio=1:0, 2:1, 1:1, 1:2, 0:1	Maximum yield of H_2-rich syngas was obtained at 700 °C and PS/HDPE ratio =1/2	[50]
MSW	Fixed bed reactor	800-900 °C, dolomite, N_2	80 vol % was achieved at 900 °C, obtained char can be used to contribute to the energy required for the process.	[51]
HDPE	Two-stages pyrolysis-catalytic steam reforming reactor	650, 750, 850 °C, N_2, different zeolite catalyst	The maximum syngas yield was achieved over Ni/ZSM5-30 catalyst, icreasing of temperature and steam feeding are favoured for H_2 production, Ni/ZSM5-30 catalyst showed excellent coke resistance and thermal stability	[52]
MSW, Waste marble powder	Fixed bed reactor	700-900 °C, 2.5-10 ml/min, N_2	The H_2 concenteration was increased with increasing the temperature and ratio of WMP to MSW. Using WMP as sorbent catalyst improved the product gas and decreased the tar content.	[53]
Waste tires	Fixed bed reactor	400-1000 °C, CO_2	Higher temperature reduced the reaction time and increased the syngas yield	[54]
Polyethylene terephthalate	Fixed bed reactor	800-950 °C, CO_2,	CO yield was increased with temperature, 95.2 wt% of the total syngas was CO at 950 °C, using of CO_2 as carrier gas can help with the management of greenhouse gas emission	[55]
Polystyrene, Paper	Semi batch tube reactor	900 °C, CO_2,	Co-gasification using CO_2 increased the total gas yield, the conversion rate was enhanced by mixing the PS with the paper, PS content of 20% increased the gas product	[56]

Table 1.2
The main conditions and conclusions for waste based syngas production (cont.)

Raw materials	**Reactors**	**Parameters**	**Main results**	**Reference**
Polyehtylene, polypropylene	RYield reactor, Aspen Plus simulator	650-1150 °C,	900 °C with steam to feed ratio of 1.5 are favourable for syngas production	[57]
Polyethylene, plastic bag, polypropylene, wood chips	Two stage fluidized bed reactor	500 °C 1st stage, 500,700, 900 °C 2nd stage, different bed materials	900 °C in the second stage was the optimim condition for H_2 in the syngas, based activated carbon produced the highest yield of H_2, while silica produced the lowest	[58]
HDPE, LDPE, PS, PET, PP	Two stage fixed bed reactor	600, 700, 800, 900 °C, CO_2, different catalyst preparation methods	The optimum syngas was obtained at 800 °C and catalyst/plastic ratio of 0.5, icreasing the rate of CO_2 input promoted the highe syngas yield, the properties and activity of catalyst was influenced by the preparation method	[59]
HDPE	One-stage fixed bed, Two-stage fixed bed reactor	500, 800 °C, N_2, CO_2, steam	The production of syngas was increased by the addition of Ni–Mg–Al catalyst and CO_2 as carrier gas, the addition of CO_2 reduced the carbon deposition, H_2 yield was increased with the addition of steam	[60]
PP	Two-stage fixed bed	500 °C 1st stage, 800 °C 2nd stage, N_2, steam	Maximum H_2 yield was obtained with Ni–Mn–Al catalyst, the interaction between Ni and catalyst support plays a significant role in the gasification process, higher rate of steam resulted in high H_2 product and less carbon depostion	[61]
HDPE, LDPE, PP, PS, PET	Two-stage fixed bed reactor	500 °C 1st stage, 800 °C 2nd stage, CO_2/steam	The optimum syngas production was reported over the CO_2/steam ratio of 4/1 and Ni-Co/Al_2O_3 catalyst, CO_2/steam ratio of 4/1 produced the highest molar ratio of H_2/CO, further addition of steam led to decreasing of the H_2/CO molar ratio	[62]

During the pyrolysis process, the polymers with long chain molecules are degrading by heating to produce smaller molecules with less complexity. Generally, pyrolysis is carried out in inert atmosphere and moderate to elevated temperature. The flexibility of process parameters is one of the features of pyrolysis process which can help to obtain the desirable products. Pyrolysis process has got more attention by many scientist due to the ability to generate an efficient amount of liquid product at moderate temperature [63]. Gas, oil and char are the main valuable products from the pyrolysis experiment. The liquid product from pyrolysis process can be utilized as fuel oil for diesel engines, turbines, boiler and furnaces [64].

In terms of green technologies, pyrolysis is the most attractive method compared to other recycling methods as the process does not produce any environmental pollutants [65]. The production of hydrogen and synthesis gas from the conversion of waste plastic has got more attention recently [66]. Due to the low yield of syngas via pyrolysis method, the syngas product would be enhanced by the combination of pyrolysis and reforming process.

Maoyun He et al, studied the gasification of waste polyethylene for syngas production over NiO/y-Al_2O_3 catalyst. Fixed bed reactor was used to investigate the effect of reaction temperature on the yield of gases. Their experiment was carried out in the presence of steam at temperature range of 700-900 °C. They found that temperature of 900°C resulted in the maximum yield of hydrogen and carbon monoxide [67]. In another study, Jon Alvarez performed the pyrolysis/gasification of mixture of waste plastic and biomass for hydrogen production using a fixed bed reactor. Ni/Al_2O_3 was introduced to the process in order to enhance the production of hydrogen and gases products. They found that increasing of plastic ratio in the feedstock with the presence of catalyst led to significant increasing of hydrogen and gas yield [68].

Using of promoters together with catalysts could enhance the catalyst performance and its stability during the decomposition reaction of waste materials (plastic and biomass). Mohamad Irfan studied the production of hydrogen-rich syngas from the gasification of MSW over Ni-CaO catalyst and HfO_2 promoter. Their results showed that the poor stability of Ni-CaO catalyst was enhanced by the addition of promter. The maximum hydrogen yield was produced with 20% ratio of HfO_2. Furthermore, a notable reduction in the amount of tar was reported over the catalyst promoter [69].

Some researches suggested that the combination of pyrolysis and gasification especially with catalyst is considered as appropriate way to produce hydrogen rich syngas with high quality [50]. Shuping Zhang et al. used high density polyethylene and pine sawdust as raw materials for the production of H_2 rich syngas from pyrolysis-catalytic gasification over mono and bimetallic catalysts. The authors observed that reaction temperature of 700 ^{o}C with plastic/biomass ratio of 2/1 were the optimal conditions for syngas production with high quality. Moreover, the maximum yield of H_2-rich syngas was obtained over bimetallic catalyst of Ni-Fe·CNF/PCs [50].

Gasification of real waste plastic was also implemented by Shan Luo Wu for hydrogen production over Co/SiO_2·HZSM-5 catalyst. Various ratio (10-30 wt%) of HZSM-5 support was used in order to investigate the catalyst performance towards hydrogen product. The authors reported that the amount of HZM-5 catalyst can affects the H_2 yield. According to their obtained results, catalyst of $Co/SiO_2{\cdot}2HZSM\text{-}5$ shows the highest activity compared to other used catalyst [70].

Increasing the reaction temperature of the second stage reactor in pyrolysis/gasification process promoted the char dry reforming and tar decomposition to smaller molecule hydrocarbons which in favour of the co-production of hydrogen and CNTs [71]. Yang et al performed the gasification of waste PP and LDPE using two stages fluidized bed reactor. Catalyst of Ni/Al-SBA-15 was placed in the first stage, while Ni-Cu/CaO-SiO_2 was placed in the second stage at temperature of 600 and 800 ^oC, respectively. The author founds that hydrogen yield was significantly increased in the second stage reactor [71] .

Using of gasification agent such as steam can improve the yield of hydrogen but also increased the energy consumption for the whole process. Instead of steam, using of wet feedstock can promoting the reactions of steam and tar reforming which leading to more H_2 product and tar reduction [72]. Therefore, direct gasification of wet MSW could increased the process efficiency [73, 74]. In another work, Guany et al used air as a gasifying agent with various experimental paramters in order to achieve the optimum hydrogen. The authors found that using a gasifying agent of air could promote the formation of gas yields (especially H_2). Moreover, residence time of 22 min and 757 ^oC were the best conditions to obtained the optimum yield of hydrogen [75]. They also reported that tar and char yield was reduced with rising the temperature to 900 ^oC. Higher temperature promoted the conversion rate of MSW and resulted in more yield of syngas and H_2.

1.6.1. Process parameters condition

The product yields and product compositions from the pyrolysis process are affected by many factors such as reactor type, reaction temperature, type and flow rate of carrier gas, residence time, pressure and type of catalyst. Controlling of these parameters can contributing to obtain the desired yield of product.

1.6.1.1. Temperature

Temperature has significant effect on the thermal decomposition of plastic material. Temperature can influence the cracking reaction of polymer chain. Increasing of reaction temperature led to increasing of cracking rate and resulting in more broken of C-C bond.

Thermogravimetric analysis (TGA) is widely used method to investigate the thermal degradation behavior of polymer materials.

Çepelipullar and Pütün [76] have investigated the thermal degradation behavior of PET using TGA. They found that PET starts to degrade at temperature of 350 °C, while the degradation of poly vinyl chloride was occurred at 220 °C. Jung et al [77] previously studied the thermal behavior of HDPE and PP. They observed that the degradation of HDPE and PP occurred at temperature range of 400-500 °C.

However, high temperature has visible effects on the thermal decomposition and product composition of plastic materials. Williams PT and Williams EA conducted the pyrolysis of LDPE using fluidized bed reactor and they reported that liquid products were decreased by increasing of pyrolysis temperature [78]. In another work, Saad et al studied the influence of process parameters on the syngas yield from the pyrolysis/gasification of waste HDPE. The process was carried out in a fixed bed reactor under two different temperatures of 500 and 800 °C. The authors reported a marked increase in the syngas yield with rising the temperature to 800 °C [60]. Furthermore, Saad and Williams investigated the influence of reaction temperature on the pyrolysis of waste plastic mixture of (HDPE, LDPE, PET, PS and PP) using fixed bed reactor at various temperature of 600, 700, 800 and 900 °C. They observed that higher syngas yield was obtained at high temperature of 800°C [59]. P.Bober has also performed the pyrolysis of waste mixture of poly ethylene terephthalate and HDPE under two different temperature of 700 and 815 °C. Their result showed that the maximum hydrogen production was achieved at 815°C [79]. Hence, it can be concluded that temperature had positive influence on the product composition of pyrolysis process especially syngas. Lower operating temperature is favoured for liquid product, while higher operating temperature is required for gaseous product.

1.6.1.2. Reactor

Choosing of reactor type is another important factor towards the pyrolysis process of waste plastic. Based on the reactor design, different reactors have different heat efficiency **(Figure 1.8)**. Moreover, to achieve a certain desired product, residence time and the mixing of catalyst and waste product are significant parameters for the selection of appropriate reactor. However, various reactors have been used for the thermal decomposition reaction of waste polymers including; batch reactor, semi batch reactor, fixed bed and fluidized bed reactor.

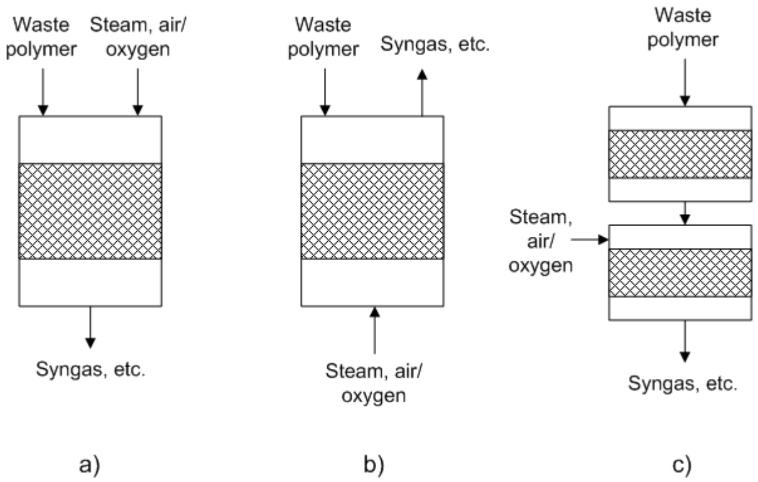


Figure 1.8
Schematic diagram of pyrolysis reactor
(a, Fixed bed reactor, b) Fluidized bed reactor, c) Two-stage reactor)

In the batch reactor type, the reaction is carried out inside closed system with no possibility for reactant addition whiles the reaction in process. On the other hand, the addition of reactant or removal of the product is possible for the semi batch reactor during the reaction. For laboratory scale applications, using of batch reactor and semi batch reactor is favoured by many researchers. The advantages of using these reactors are represented by the simple design, high conversion of reactants and the easily of controlling of operating conditions [80-84]. While, the high labor cost and the difficulty of large scale applications are the disadvantage of theses reactors [85].

Sakata et al. [86] studied the thermal and catalytic pyrolysis of waste mixture of HDPE and PP in a batch reactor at temperature of 380 and 430 °C. Catalytic pyrolysis using batch and semi batch reactors are suffering from the formation of coke on the catalyst surface which can hinder the efficiency of catalyst after a particular time. A semi batch reactor was used by Abbas-Abadi et al. [87] to perform the pyrolysis of PP at 450 ^{o}C. Ahmed and Gupta have used a batch reactor at 600 °C to produce syngas from the gasification of cardboard [88].

Regarding to fixed bed reactor, a regular particle size of waste plastics are feed to the reactor and the catalysts are placed in a static bed. Irregular shape of plastic particles may cause some problems during the feedstock feeding. Hence, many researchers have used the fixed bed reactor for the two step pyrolysis as the products (gas and liquid) from the first reactor can feed to the fixed bed reactor without any feeding problems [85]. A two stage fixed bed reactor was used by Saad and Williams to conducted the catalytic pyrolysis of waste plastic for syngas production [59].

For the fluidized bed reactor, distributer plate is used to place the catalyst inside the reactor. Reactants with the fluidize gas are pass through the distributer and mixed with the catalyst. Fluidized bed reactor is favoured by many researches due to its efficiency for heat transfer and more flexible compared to batch reactor [89, 90]. G.Ruoppolo et al have studied the gasification of plastic and biomass mixture for hydrogen rich syngas production in a fluidized bed reactor at 780 °C [91].

1.6.1.3. Pressure and residence time

Pressure and residence time have significant impact on the product distribution of pyrolysis process [92]. At certain pyrolysis temperature, increasing of process pressure resulted in more gaseous products. According to the literature by Murata et al. [93], who conducted the pyrolysis of HDPE at pressure range of 0.1-0.8 MPa, a clear increasing of gases yields were reported when the process pressure was increased to 0.8 MPa. Moreover, the formation of double bond is effected by the pressure. Increasing of pressure led to decreasing of C-C bond of polymer materials during the thermal decomposition [93].

Regarding to the effect of residence time, long residence time has positive effect on the light hydrocarbons in the product yield. The more time that waste particles spend inside the reactor, the more conversion of primary products [94]. The influence of residence time on the pyrolysis of waste plastic was investigated by Mastral et al. [95]. They reported a correlation between the residence time and the temperature of the reactor as the high pyrolysis temperature could reduce the effect of residence time on the product yields (gas and oil). Moreover, lower reaction temperature with long residence time led to increasing of oil product. Thus, it can be noticed that the influence of residence time and pressure are affected by the temperature. Additionally, more studies are considered that temperature is the essential factor because most of pyrolysis processes are carried out at atmospheric pressure.

1.6.1.4. Catalyst

Catalyst plays a significant role in the pyrolysis of waste plastic and other waste materials. Pyrolysis is known as endothermic process which required high temperature to carry out. Catalyst can reduce the high energy required for the process, due to the reducetion of the activation energy of the process. Moreover, using of catalyst enhanced the conversion rate and speeds up the thermal decomposition of waste plastics in the process. However, many catalysts have been utilized for the pyrolysis of waste plastics. Zeolite, silica-alumina and FCC catalyst are the commonest for the decomposition reaction of theses wastes. In addition, the influences of catalyst types on the product yield from the pyrolysis process have been investigated by many researchers. **Table 1.3** summarizes the effect of catalysts using different feedstocks to the product properties.

Table 1.3
Different catalyst type for waste decomposition using various feedstocks

Raw materials	Catalyst	Results	Reference
HDPE, LDPE, PET, PP and PS	Mabisan clay, showedanng clay, dolomite and zinc oxide	Mabisan clay catalyst produced the maximum yield	[96]
Real waste plastics	Ni/Al_2O_3 and $Ni\text{-}CO/Al_2O_3$	Ni/Al_2O_3 produced the maximum yield	[97]
HDPE, LDPE,PP and PS	Ni-Fe	Catalyst thermal stability was improved by introducing the Ni	[98]
Waste plastic and biomass mixture	HZSM-5	Product yield was increased by catalyst	[99]
Waste plastic and biomass	Ni/Al_2O_3	Hydrogen and gas yield was improved by catalyst	[68]
LDPE	Ni, Co, Ni-Mo, Co-Mo with natural zeolite	Co-Mo/zeolite catalyst resulted in more conversion of LDPE	[100]
PP	Ce, Zn, Ca, Mn and Zn with Ni based	Ni-Mn-Al catalyst produced the maximum H_2 yield	[61]
LDPE/HDPE	Ni/ZSM-5-30, Ni/β-zeolite and Ni/Y-zeolite-30	Ni/ZSM-5-30 catalyst produced the maximum syngas yeild	[52]

Khaing et al. studied the influence of different catalyst type on the liquid product from the pyrolysis of mixed plastic mixture of HDPE, LDPE, PET, PP and PS. Mabisan clay, showedanng clay, dolomite and zinc oxide were used as a catalyst in a fixed bed reactor. They reported that the maximum pyrolysis oil (67.06%) was achieved over Mabisan clay catalyst [96]. Saad and Williams conducted the pyrolysis of various mixed plastic over Ni/Al_2O_3 and $Ni\text{-}Co/Al_2O_3$ catalysts. Rising-pH technique was used for the preparation of catalysts. Their results showed that catalyst of Ni/Al_2O_3 produce the highest yield of syngas product (153.67 mmol/g) [97].

Yao et al. examined the effect of various ratios of Ni-Fe catalyst on the hydrogen production from the pyrolysis of HDPE, LDPE, PP and PS. The authors found that catalyst thermal stability was improved by introducing the Ni. Moreover, the composition of catalyst has great impact on the quality and amount of the produced CNTs [98].

Alvarez et al conducted the pyrolysis-gasification of plastics and biomass in a fixed bed reactor. They found that hydrogen and gas yield was improved by introducing the Ni/Al_2O_3 catalyst to the process [68].

Bi-functional catalyst of Ni, Co, Ni-Mo, Co-Mo have been investigated by Sriningsih et al. [100] for the fuel production from waste LDPE. Natural zeolite was used as catalyst support which was refluxed in hydrochloric acid then dried in an oven. A microwave was used for heated up the metal/loaded catalysts and hydrogen gas was used for the reduction. The authors found that higher conversion of LDPE was achieved over Co-Mo/zeolite catalyst at temperature of 350 ^oC.

The influence of different metal addition to nickel based catalyst on the H_2 yield from the waste PP pyrolysis have been studied by Nahil et al. [61]. Various metals of Ce, Zn, Ca, Mn and Zn were added to Ni based catalyst. Catalysts were prepared by using co-precipitation method. Among the various used Ni-metal catalysts, Ni-Mn-Al catalyst showed the best performance in terms of hydrogen production.

Different types of zeolite supported Ni catalysts have been investigated for the syngas production from pyrolysis of waste polyethylene. ZSM-5-30, β-zeolite and Y-zeolite-30 catalysts were impregnated with nickel and examined for the production of hydrogen/syngas. The authors found that the maxiumum syngas yield (100.72 mmol/g) was obtained in the presence of Ni/ZSM-5-30 catalyst [52].

Saad et al. conducted the catalytic pyrolysis of waste plastic mixture of LDPE, HDPE, PET, PS and PP focusing on the influence of process parameters on the syngas yield. Catalyst of $Ni\text{-}Co\text{-}Al_2O_3$ was used in this expirement in order to enhance the product yields. Two different methods were used for catalyst preparation and the influnce of catalyst preparation method on the syngas yield was also studied. Their results showed that the syngas production was higher by using rising-pH technique for catalyst preparation compared to the catalyst prepared by impregination method [59].

Zhang and Williams have performed the catalytic pyrolysis of waste tyres for hydrogen and carbon nanotubes production over Ni/Al_2O_3 catalyst. A wetness impregnation method was used for catalyst preparation for the expirement. Ethanol was used for disolved the nickel-nitrate then the alumina support was added to the solution of nickel nitrate and ethanol. The authors demonstated that maximum hydrogen yield was obtained with tyre:catalyst ratio of 1:1 and reaction temperature of 900 ^oC [101].

1.6.1.5. Reaction atmosphere

The product yields and compositions from pyrolysis-gasification of waste plastic are significantly affected by the type of reaction atmosphere and carrier gas. There are many types of gases that can be used as atmosphere for the decomposition reaction of waste plastics such as carbon dioxide, oxygen, hydrogen, nitrogen, steam, etc. these kind of atmosphere have visible influence on the product distribution from pyrolysis-gasification process. In addition, the type of atmosphere reaction can also influence the coke and tar formation. **Table 1.4** summarizes the different pyrolysis-gasification processes using various raw materials and reaction atmospheres.

Table 1.4
The main pyrolysis-gasification processes of waste polymer decomposition using different raw materials and reaction atmosphere

Raw materials	**Catalyst**	**Atmosphere**	**Reactor**	**Refrence**
LDPE, PP	-	Hydrogen	Batch reactor	[102]
LDPE, HDPE, PP, PS, and PET	Zeolite	Hydrogen	Micro-pyrolyzer reactor	[103]
HDPE, PET, PS, PP and PE	Ni/Al_2O_3, $Ni-Co/Al_2O_3$	Carbon dioxide	Two stages fixed bed reactor	[97]
Biomass	Fe_2O_3	Oxygen	Fixed bed reactor	[104]
HDPE, LDPE, PP, PS and PET	$Ni-Co-Al_2O_3$	Carbon dioxide	Two stages fixed bed reactor	[59]
Biomass	Dolomite	Oxygen	Fluidized bed reactor	[105]
HDPE, LDPE, PP and PET	Me-Ni/ZSM-5 (Me=Ca,Ce,La,Mg,,Mn)	Nitogen/Oxygen	Two stages tubular reactor	[106]
HDPE	Ni/Zeolite	Steam/N_2	Ttwo-stage steam reforming Reactor	[52]

Escola et al. [102] conducted the thermal cracking of polyethylene in the presence of hydrogen as reaction atmosphere. They found that hydrogen can minimize the formation of olefin as the products with double bonds are saturated with H_2. Yuan Xue et al. [103] also studied the effect of hydrogen atmosphere on the catalytic pyrolysis of waste plastic mixture of (PE, PP, PS, and PET). The authors reported that using of hydrogen as carrier gas can increased the yield of hydrocarbons and decreasing of solid residue.

Carbon dioxide as carrier gas can also influenced the product yield and product composition from pyrolysis-gasification of waste plastics. A study conducted by Saad and Williams [97] to investigate the effect of CO_2 atmosphere on the decomposition reaction of waste plastic mixture. Their obtained results showed that using of CO_2 atmosphere promoted the dry reformaing reaction wthic resulted in more yield of hydrogen and CO. The influence of carbon dioxide on the catalytic reforming of (HDPE, LDPE, PP, PS and PET) was also examined by Saad and Williams. The authors demonistrted that the higer rate input of CO_2 led to significant increasing of syngas production [59].

Additionally, oxygen can be utilized for partial oxidation in the decomposition reaction of waste plastic. The ratio of O_2 atmosphere can greatly influenced the product yield (syngas) from the pyrolysis-gasification of waste polymers. Previously, Zhifeng Hu et al. studied the influence of oxygen atmosphere content on the the syngas production from microalgae. Their obtained data demonistrated that using of oxygen atmosphere could enhance the formation of hydrogen and carbon monoxide [104]. Al-asadi et al. [106] reported that positive effect in the gas and liquid yields was found by increasing the ratio of oxygen atmosphere for the gasification process of HDPE, LDPE, PP and PET. Besides, the using of oxygen atmosphere not only enhance the pyrolysis-gasification products but also reduced the concentration of tar [105].

Steam as a gasification agent has been used widely for the production of hydrogen rich syngas from waste plastics. The addition of steam into the process of pyrolysis-gasification can significantly influenced the decompoaition reaction of waste polymers. The presence of steam can promoted the formation of gases especially hydrogen due to the more reforming reactions of methane and water gas shift reaction [107]. Furthermore, the required heat for the process can be supplied throw the the reforming reaction itself as the steam gasification is known as endothermic reaction [108]. Wu and Williams [109] conducted the pyrolysis-gasification of waste polypropylene in a two stages reactor with steam over Ni/CeO/ZSM-5 catalyst. The authors reported that hydrogen yield was enhanced by the steam reforming of the produced gases from the pyrolysis process in the first stage.

1.6.2. Kinetic parameters

In order to understand the thermal degradation behaviour of plastic, studying the kinetic parameters is one of the significant factors for better recycling of waste plastic. Also, the investigation of pastic degredation parameters is a crucial step for the process reactor design. Moreover, the many reactions of plastic decomposition can add more complexity to the process [110]. Hence, the product yields from pyrolysis/gasification process can be enhanced as a result of the proper reactor desing and better understanding of decomposition reactions. Various analytical methods have been applied to figure out the reaction pathway of plastic degredation such as thermogravimetric analysis [111-113]. TGA can provide suffiecnt informations about the complex reactions of thermal plastic degradation. **Table 1.5** summarizes the main reaction kinetic parameters of waste polymer decomposition using different raw materials and reaction conditions.

Table 1.5
The main reaction kinetic parameters of waste polymer decomposition using different raw materials and reaction conditions [114]

Kinetic approach	Method	Raw material	E_a (kJ/mol)	Reference
Ozawa-Flynn-Wall and the Kissinger-Akahira-Sunose methods	TGA, N_2 atmosphere	Refuse derived fuel	75-212	[115]
	TGA, Ar atmosphere	PP, LDPE, HDPE, PVC, PET	334-364	[116]
	TGA-FTIR, Py-GC/ MS, N_2 atmosphere	Kitchen waste, waste tire	198- 252	[117]
	TGA/MS/FTIR, N_2 atmosphere	Cherry seed, PVC	145-245	[118]
	TGA, N_2 atmosphere	Chlorella vulgaris biomass	138-158	[119]
	TGA, Ar atmosphere	Bamboo sawdust, LLDPE	143-400	[120]
	TGA, N_2 atmosphere	PET, Samanea saman seeds	130-179	[121]
Lumping approach	Tubular laboratory cracker	LDPE and a heavy petroleum residue fraction	147-313	[122]
	Two stage laboratory scale batch reactor using, N_2 atmosphere	HDPE, PP, LDPE	33-318	[123]
	Two stage laboratory scale batch reactor using, N_2 atmosphere	Real waste plastics	86-394	[124]
Distributed activation energy model	TGA, N_2 atmosphere	Lignocellulosic biomass, waste tyre, PLA, PS, PET, PP, HDPE	236-362	[125]
	TG-FTIR, N_2 atmosphere	PE, PP, PVC, rubber, textile, paper, poplar wood, pork and rice	124-313	[126]

Table 1.5
The main reaction kinetic parameters of waste polymer decomposition using different raw materials and reaction conditions [114] (cont.)

Kinetic approach	Method	Raw material	E_a (kJ/mol)	Reference
Multi-stage kinetics model	TGA, N_2 atmosphere	YW, FW, textile, paper, rubber, LDPE, HDPE, PP, PET and PS	75-324	[127]
Starink´s model, model-based kinetics	TGA, Py-GC/MS, N_2 atmosphere	Waste tires	102-177	[128]
Dynamic mechanism function	3-stage pyrolysis, TGA, FTIR, N_2 atmosphere	Polyethylene, cornstalk and anthracite coal	107-210	[129]
First and third-order chemical reactions	TGA, N_2 atmosphere	Food waste (lignin, bone and plastic)	29-114	[130]

The investigation on the thermal degradation kinetics of waste plastic has been carried out by many reseachers [131, 132]. Some literature reported that product yields from the decomposition of single waste plastic are differ from the yields of mixture plastic waste [133]. This fact proved that during the decomposition reaction, the initial products from each single plastic in the waste mixture can react with other products from other plastics.

The required activation energy for the conversion of waste plastic can be reduced by the application of catalyst [134, 135]. Thermogravimetric technique was applied by Marcilla et al for the catalytic pyrolysis of waste mixture of HDPE and PP and the obtained results were compared with thermal pyrolysis. The authors reported that the maximum decomposition temperature was reduced by using catalysts and more conversion rate was obtained [136].

1.6.3. Pyrolysis products

The decomposition of plastic wastes by pyrolysis process produces three main products which are oil, gases and char. As mentioined before, the process parameters such as temperature, residence time, reactor type, pressure, etc can affects the proportion of the product yields.

1.6.3.1. Pyrolysis oil

Pyrolysis oil is one of the three major valuable products from the converting of waste plastics. Oil product from pyrolysis process are effected by many factors such as temperature, heating rate, ash content and volatile matter [137]. High content of ash reduced the amount of liquid yield, while high volatile matter increased the amount of pyrolysis oil. However, the amount of gaseous product and char formation are increased as a consequnce of oil decreasing. Pyrolysis oil is also influenced by the type of plastic, for example; PET has higher oil yield compared to PVC [138]. Oil extracted from wastes can be used as fuel after quality improvement as it contains a mixture of hydrocarbons from the range of kerosene and petrol [139].

1.6.3.2. Gases

The production of gases from pyrolysis process is higly depending on the temperature and type of waste plastic. In general, long residence time with elevated temperature are the best conditions for gases yield [140]. These parameters have opposite impact on the pyrolysis oil. Onwudili et al [141] studied the influnce of plastic type and reaction temperature on the pyrolysis of individual waste LDPE and PS and their mixture. Their obtained results showed that the mixture of LDPE and PS generated more gases yield compared to individual waste. Also they reported that rising the temperature from 350 to 450 ^{o}C resulted in more gases product. Regarding to plastic type, PET and PVC produced more gases product compared to the other waste plastics.

As mentioned above, plastics are rich in hydrocarbons therefore, the production of syngas (H_2 and CO) from waste plastic using pyrolysis-gasification processes have been reported by many studies [84, 142, 143]. The syngas are formed by the recombines of the volatile product from pyrolysis and gasification processes. Gasification of waste plastic is considered as a novel route for the production of H_2-rich syngas as most of industrial processes are based on fossil fuels for hydrogen production [144]. The production of syngas are highly influenced by the process paramters such as temperature, catalyst and atmosphere type. Moreover, the type of raw materials or feedstock is also affected the syngas yield in the pyrolysis-gasification process. However, the presence of catalyst with high temperature can promote the more decomposition rate of raw materials and resulting in more syngas product.

Many researches have sutided the production of synthesis gas from waste plastic. Shan-Luo et al. [70] conducted the production of syngas from gasification of waste plastic using polyethylene waste in the presence of Co/SiO_2@HZSM-5 catalyst. In another work, Yao et al. [52] investigated the production of H_2-rich syngas from waste polyethylene by gasification with steam. They reported that hydrogen from catalytic reforming of waste

PE was increased with increasing of steam rate and temperature. Additionally, syngas can be produced from the combination of waste plastic and biomass. Déparrois et al. [56] studied the co-gasification of polystyrene with paper for syngas production. The authors reported that co-pyrolysis or co-gasification have positive effect on the syngas yield as the amount of hydrogen product was doubled due to the synergistic influence on cracking reactions.

1.6.3.3. Char

Char is a carbonaceous materials formed as by-product from the plastic degredation. Process conditions of low reaction temperature, long residence time can increased the char yield in pyrolysis process. The size of feedstock particles can also influenced the type of produced char as the large size produced tough char while the smaller size of particle feedstock produced a finer char. The chemical and physical properties are effected by the presence of inorganic species [145]. Char can be utilized in the production of carbon nanotubes and activated carbon after catalytic pretreatment [146]. Jamradloedluk et al. [147] investigated the char composition from waste HDPE. Their results showed that the obtained char was mainly contained fixed carbon and volatile matter (97 %). Although higher temperature resulted in lower amount of char yield. A study conducted by Jung et al. [77] showed that char yield form pyrolysis of waste PP and PE was increased with temperature. Char has a calorific value of 18.8 MJ/kg. Char can be used in combustion due to its lower sulphur content. Moreover, it can be utilized in upgrading process to remove the heavy metals from water.

1.6.3.4. Carbon nanotubes (CNTs)

Table 1.6 shows the main products from pyrolysis-gasification processes of waste polymer decomposition using different raw materials and reaction atmosphere. Carbon nanotubes are another by-product from pyrolysis-gasification of waste plastic materials. The type and amount of carbon nanotubes are affected by the process paramters and expirement conditions. Carbon nanotubes are considered as unique materials as it has thermal, mechanical and electrical stability [160, 161]. Hence, its recived more attention recently. Gasification of waste plastic is the most suitable way for production of CNTs as the process can produce hydrogen together with carbon nanotubes.

Table 1.6
The main products from pyrolysis-gasification processes of waste polymer decomposition using different raw materials and reaction atmosphere

Raw materials	Carrier gas	Catalyst	Product	Refrence
LDPE, HDPE, PP, PS, PET	He, H_2	HZSM-5	Oil	[103]
HDPE	He	FeO_3, CoC, ZnO, MnO_2, NiO	Oil	[148]
LDPE, PP, HDPE	N_2	Without	Oil, Gaseous	[149]
HDPE, Switchgrass	N_2	HZSM-5	Oil	[150]
PE, PP, PS, PET	Steam	CaO, $Ca(OH)_2$	Oil, Gas	[151]
HDPE, PMMA	N_2	Ni, Co	H_2	[79]
PET, Waste tires, biomass	Steam, O_2, Air	y-Al_2O_3, Ni/y-Al_2O_3	Syngas	[152]
Plastic/Biomass	N_2	Ni/y-alumina	H_2-syngas	[91]
HDPE, LDPE, PS	Ar	Ni-Fe	H_2, CNTs	[98]
PP	N_2, H_2O	Ni/Mn/Al	H_2, CNTs	[153]
LLDPE	N_2	Ni_2O_3	CNTs	[154]
PP	N_2	HZSM-5	H_2, CNTs	[155]
HDPE, PP, PS, PVC, PET	N_2	Ni/Mo/MgO	H_2, CNTs	[156]
LDPE, PP, PS	N_2	Ni/Al	H_2, CNTs	[157]
LDPE	N_2	Fe/Al	H_2, CNTs	[158]
PP	Ar/H_2	Ni	CNTs	[159]

The presence of catalyst in the decomposition reaction of waste plastic can enhance the yield of CNTs. Nahil et al. [61] investigated the production of CNTs through gasification of waste polypropylene in the presence of Ni-based catalyst. Their obtained results showed that CNTs quality was improved by the lower injection of steam rate. Furthermore, nickel based catalyst of Ni/Mn/Al showed a promising result in terms of CNTs and hydrogen production. Temperature of reaction also influenced the production of CNTs. A study conducted by Yang et al. [71] reported that reactor temperature of 800 °C are favoured for the production of CNTs and hydrogen as the higher temperature increased the formation of hydrocarbons with smaller molecule that promoting the production of hydrogen and CNTs.

1.6.4. Economic issues

Hydrogen and syngas should be produced in an economic way in order to share the competition with the conventional fuel in the market. Price differentional between syngas/hydrogen and crude oil is the most significant factor for economic potential of hydrogen syngas. In order to obtain a clean and economice fuel, some factors should be taken into consideration. Syngas/hydrogen production, distribution and instiallation of required sites are essential factor the estimation of the cost. For example, the cost for hydrogen delivery was high in the first decade as it cost more than 10 euro for each one kilogram. Therefore, the hydrogen cost was higher and most economic challenging. Hydrogen/syngas cost is higly depending on their utilization which can be droped with more increasing of application. Ball and Weeda have reported that delivery cost for hydrogen was dropped from 10 to 7 €/kg due to the increasing of hydrogen cars and utilization [162].

1.6.5. Scaled-up, pilot processes

Syngas from waste plastic was already produced using large scale technologies. The first large scale process was carried out in the US with production of 10 tones per day [163]. **Table 1.7** shows the main properties of the scaled-up processes for waste based syngas production.

Table 1.7
The main properties of the scaled-up processes for waste based syngas production

Process	Raw materials	Parameters	Product	Reference
Gassification using pilot-scale	MSW	450-1200 °C, air	Syngas	[164]
Gasification using pilot plant	MSW	700-800 °C, steam, oxygen	Syngas	[164]
Gasification using rotary kiln pilot plant	Waste tyres	400-1100 °C, steam,	Syngas	[165]
Gassification using pilot-scale	Biomass	800 °C, oxygen-enriched air and steam	Syngas	[166]
Gassification using pilot-scale	Solid Recovered Fuel from MSW	700 °C, air,	Syngas	[167]
Gassification using pilot-scale	Lignin pellets	850 °C, steam, N_2, dolomite	Syngas	[168]
Gassification using pilot plant	MSW, orujillo, meat and bone meal dried sewage sludge	770-870 °C, air	Syngas, CH_4	[169]
Gassification using large scale pilot	Solid waste	N_2, CO_2, steam and air	Syngas	[170]
Gassification using pilot- scale	Biomass	780-800 °C, air	Hydrogen-rich gas	[171]
Co-gassification using pilot-scale	forest residue and wood charcoal	1000 °C, air	Syngas	[172]
Gassification using pilot-scale	Wood pellets	200-1000 °C, steam, air	Syngas	[173]

Texaco gasification and Waste Gas Technology UK limited processes are examples of the most common technologies for syngas production with pilot process. Various types of waste materials can be fed to these processes to produce the syngas. In this process, the waste materials are first dried and granulated to the suitable size then feed to the reactor. A cylindrical reactor is used for carried out the gasification process at reaction temperature from 700 to 900 ^{o}C. The Texaco gasification process was performed in the presence of steam and oxygen at high temperature of 1200-1500 ^{o}C [174].

A study conducted by Gerhard Hirm in Germany reported that 50,000 tones/year of plastic wastes are converted to syngas by using gasification process in a large scale pilot plant. Air was used for the partial oxidation and pyrolysis of waste plastic materials. The reaction of pyrolysis was carried out at temperature of 450-1200 ^{o}C. Hot gas filters were used to clean up the produced syngas. After cleaning step, the syngas was cooled down and ready to use [175].

In another work, a rotary kiln gasifier was used in pilot plant to produce high energy syngas from waste tyres [165]. 5 kg/h of raw materilas were feeded with steam to the continuous pilot plant at temperature range of 400 to 1100 °C. The authors used a treatment system to remove the char particles from the produced syngas.

1.6.6. Challenge, unsolved problems

Pyrolysis and gasification processes are facing some technical and environmental challenges. The availability of feedstock in large quantity and steady flow is one of the technical challenges in the pyrolysis process as many contries export their waste abroad. Therefore, waste plastic supplier is important factor towards a good economic pyrolysis. Plastic wastes are differing in shape based on their origin and source. Moreover, these wastes may be contaminated with other materials. The presence of contaminants in the raw materials may converting to the yields which affect the quality of pyrolysis products [53]. Hence, it’s a chellenge to feed waste plastic to the process before a pretreatment step to remove the contaminants as. Furthermore, a crushing step of plastic waste is required to ensure a uniform or suitable size for some pyrolysis reactors. These steps will add more cost to the whole process. The characterization of feedstock is another challenge for pyrolysis process as the waste plastic comes from different sources which may contain some toxic substance. These poisoning materials may release from the process and cause a serious environmental and health problems [176]. In addition to the above challenges, the products from gasification and pyrolysis process conatin halogens, alkaline and tar. These components cause some operational and environmental problems [177].

1.7. Future trends for waste to syngas processes

Waste plastics are materials with high energy content. Many environmental problems related with waste treatment via conventional recycling method such as incineration and landfill. The application of new technologies for waste treatment have gained more attention in the international market due to the ability of these techniques to recover and transform the unwanted waste to high value products such as syngas. Syngas from waste treatment can be utilized in chemical synthesis, engines, fuel cells, turbines and boilers. Hence, the waste plastic could be a good commodity to be sold in the international markets. United Kingdom was already shifted their policy to the production of sustainable and clean energy in order to mitigate the climate change [178]. 14 plants were built up in UK alone for the production of energy from waste treatment using gasification process.

1.8. Main finding of litartures focussing to waste based syngas production

According to literature, fossile fules are still the main source of energy for the worldwide. In one hand, this type of energy have many serious problems which can affects the human health and environment. On the other hand, it is non-renewable ener-gy and will be exist in the future. Therefore, finding an alternative and renewable source for energy have gained more attention recently. Various afforts have been applied by secnitiest and reserachers in order to minimize the depends on these fuels. Syngas is one of the promising energy that can share the world energy demand. The converting of waste plastics materials into useful products such as syngas (H_2 and CO) could meet the energy requirement and mitigate the depends on fossile fuels as energy source. Morover, it can help to decrease the waste accumulation and save the envrionment from their impacts.

Different techniques have been applied for converting of waste plastic into valuble products such as syngas. Waste to energy techniques via pyrolysis and gasification ara considered as the most environmental method. These techniques are effected by many paramters such temperature, residence time, carrier gas and catalyst type. However, converting of waste plastic into syngas are facing some challenges such as cost due to the prior treatment steps (cleaning, sepration and crushing). To handle with such challenges, we used real waste plastic mixture to avoid the additional treatment steps and obtained an economic process.

Based on the recent reviews, the development of new modified catalysts could enhance the production of syngas. Some researchers suggest that using of cheap catalyst with high catalytic activity such as nickel based catalysts could be the most approprite choise for pyrolysis-gasification process. Moreover, the catalyst activity can be improved by using of second metal promoters. However, there is lack of information about the effect of second metal promoters on the catalyst performance for the decomposition of real waste plastic. Morover, there are a few refrences about the combination of second promoters (Ca, Ce, La, Mg, and Mn) with nickel. Hence, our main objective is to investigate the influence of the modified catalysts towards the pyrolysis-gasification of waste plastic mixture. Addi-tionally, using of different carrier gas such as carbon dioxide could helps in CO_2 capture processes and decreasing of CO_2 emission in the atmosphere.

2. EXPERIMENTAL PART

According to the literature, many reasearches have been studied the influence of different process paramters and conditions on the product yield and compositions form pyrolysis/gasification of plastic waste. Various catalysts with different supportes have been examined for that purpose. However, it is uncertain whether the application of second metal can enhance the catalyst activity as there is lack of information about the effect of second metal promoters on the catalyst performance for pyrolysis and gasification of waste plastic. Hence, the goal of this study is to investigate the effect of the modified catalysts towards the pyrolysisgasification in order to obtan the optimum condition for hydrogen and syngas yields. Moreover, different expiremental paramters were studied for better conversion rate of feedstock.

2.1. Materials

2.1.1. Raw materials

A mixture of real waste plastics obtained from municipal sources in Hungary were used as raw materials for this work. The type of plastic in the waste mixture was investigated by FTIR spectroscopy based on its infrared spectra. The composition of these wastes were 45% PET, 19% PP, 17% LDPE, 14% HDPE and 5% others (polystyrene, ethylene-propylene copolymer) **(Table 2.1)** [179].

Table 2.1
The main properties of the raw material

Property	**Value**
Source	Real waste
Composition	45% PET, 19% PP, 17% LDPE, 14% HDPE, 5% other
Volatile, %	93.3
Fixed carbon, %	3.7
Ash, %	2.3
Moisture, %	0.8
C, %	71.6
H, %	11.4
N, %	0.8
O[a], %	16.2

[a] *by difference*

Laboratory grinder (Dipre GRS 183A9) was used for milling the raw materials into small particles (<5mm). **Figure 2.1** shows the apparence of the used raw material. Based on the results of the proximate and ultimate analyses, raw materials contain 71.6% of carbon, 11.4% of hydrogen, 16.2% of oxygen and 0.8% of nitrogen. The fixed carbon and ash content of the raw material was 3.7 and 2.3%, respectively [179].

Figure 2.1
The appearance of the raw material

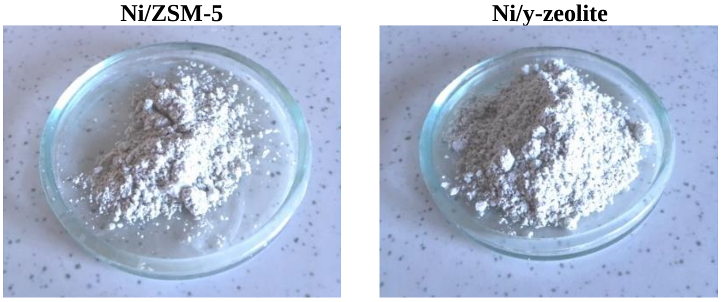
2.1.2. Catalysts preparation and characterization

In this chapter the methods for the catalysts modifications and characterizations are descriebed. A Fritsch Analysette 22 instrument based on Fraunhofer theory was used to investigate the average grain diameter of each catalyst. While, the morphology of the catalysts was analyzed by nitrogen adsorption/desorption isotherms using Micromeritics ASAP 2000 instrument. BET method was used to determine the surface areas based on nitrogen adsorption isotherms, while the BJH surface was calculated using the nitrogen desorption isotherms based on the BJH model. The morphology and elemental composition of the catalysts were investigated by Scanning Electron Microscopy (FEI Thermo Fisher Apreo S LoVac instrument, EDAX AMETEK Octane Elect Plus).

2.1.2.1. Ni modified zeolite catalysts for catalyst supporter selection

In the first section of the thesis, the effects of various supporters of zeolite catalysts were investigated: ZSM-5, y-zeolite, β-zeolite and natural zeolite. The neat catalysts were loaded by Ni using wet impregnation method according to the following steps. The catalyst supporters had been added into 1M $Ni(NO_3)_2{\cdot}6H_2O$ dissolution and continuously stirred for 2 hours at 85 °C. Then catalysts were dried for 10 hours at 110°C, and each of them was conditioned at 650 °C for 4.5 hours in air. The nickel content of each catalyst was measured by x-ray analysis. Ni/ZSM-5, Ni/y-zeolite, Ni/β-zeolite and Ni/natural zeolite catalysts had nickel content of 10.4, 10.1, 10.3 and 10.7% [180]. The appearance and the main properties of the catalysts are shown and summarized in **Figure 2.2 and Table 2.2.**

Ni/ZSM-5 **Ni/y-zeolite**



Ni/β-zeolite **Ni/natural zeolite**

Figure 2.2
The apparence of the catalysts

Catalysts were in powder form with average diameter of 19.5-38.2μm. Ni/y-zeolite had the largest BET surface, while Ni/natural zeolite the smallest. Regarding the Ni content, it was in the range of 10.1 and 10.7%.

Table 2.2
The main properties of the catalysts [180]

	Ni/ZSM-5	**Ni/y-zeolite**	**Ni/β-zeolite**	**Ni/natural zeolite**
Apperence	powder	powder	powder	powder
Average grain diameter (μm)	19.5	15.1	20.6	38.2
S_{BET}, m^2/g	315	610	580	205
S_{BJH}, m^2/g	109	215	118	72
Nickel content %	10.4	10.1	10.3	10.7

2.1.2.2. Me/ZSM-5 (Me=Ni, Co, Fe (II), V, Zn) catalysts with different Si/Al ratio

Based on the results of catalyst supporter selection, ZSM-5 synthetic zeolite was selected for further investigation. Because of not only the catalyst pore structure, but also the Si/Al ratio can significantly affect their role, ZSM-5 synthetic zeolites with different silica/alumina ratios were modified and investigated. Firstly the neat ZSM-5 catalysts were modified by Ni, Co, Fe(II), V and Zn using the previously descriebed wet impregnation method. 1M $Ni(NO_3)_2.6H_2O$, $CoSO_4.7H_2O$, $FeSO_4.7H_2O$, V-EDTA, $ZnCl_2$ dissolution was used for the catalyst impregnation [181]. The main properties of the modified catalysts are summarized in **Table 2.3-2.5.**

Table 2.3
The main properties of the catalysts (neat ZSM-5, Si/Al=22.5)

	Ni/ZSM-5	**Co/ZSM-5**	**Fe/ZSM-5**	**V/ ZSM-5**	**Zn/ ZSM-5**
Apperence	powder	powder	powder	powder	powder
Average grain diameter (µm)	15.5	33.8	38.2	30.2	39.5
S_{BET}, m^2/g	361	345	332	331	348
S_{BJH}, m^2/g	81	80	78	80	80
Metal content, %	11.5	9.4	10.8	11.2	10.2
Si/Al	21.8	22.1	21.9	22.3	22.4

Table 2.4
The main properties of the catalysts (neat ZSM-5, Si/Al=41.9)

	Ni/ZSM-5	**Co/ZSM-5**	**Fe/ZSM-5**	**V/ ZSM-5**	**Zn/ ZSM-5**
Apperence	powder	powder	powder	powder	powder
Average grain diameter (µm)	12.1	28.5	38.2	35.1	32.4
S_{BET}, m^2/g	382	366	368	372	357
S_{BJH}, m^2/g	98	95	97	98	96
Metal content, %	11.0	11.3	11.2	10.3	10.7
Si/Al	42.1	41.5	41.7	41.6	41.1

Table 2.5
The main properties of the catalysts (neat ZSM-5, Si/Al= 65.5)

	Ni/ZSM-5	**Co/ZSM-5**	**Fe/ZSM-5**	**V/ ZSM-5**	**Zn/ ZSM-5**
Apperence	powder	powder	powder	powder	powder
Average grain diameter (µm)	16.8	22.4	20.6	22.5	21.7
S_{BET}, m^2/g	376	352	358	360	354
S_{BJH}, m^2/g	115	110	106	114	111
Metal content, %	10.2	10.5	10.8	10.3	10.8
Si/Al	65.1	65.6	65.3	64.9	65.1

As shown in ***Table 2.2***, Ni/ZSM-5 catalyst has the highest surface area among the other used catalysts. The S_{BET} for Ni/ZSM-5 catalyst was 361 m^2/g, while V/ZSM-5 had the lowest S_{BET} for the catalyst with Si/Al of 22.5. On the other hand, the average grain diameter was the lowest for Ni/ZSM-5 catalyst. At Si/Al ratio of 41.9, Fe/ZSM-5 catalyst had the highest average grain diameter (38.2). The appearance of the synthetized catalysts are shown in **Figure 2.3**.

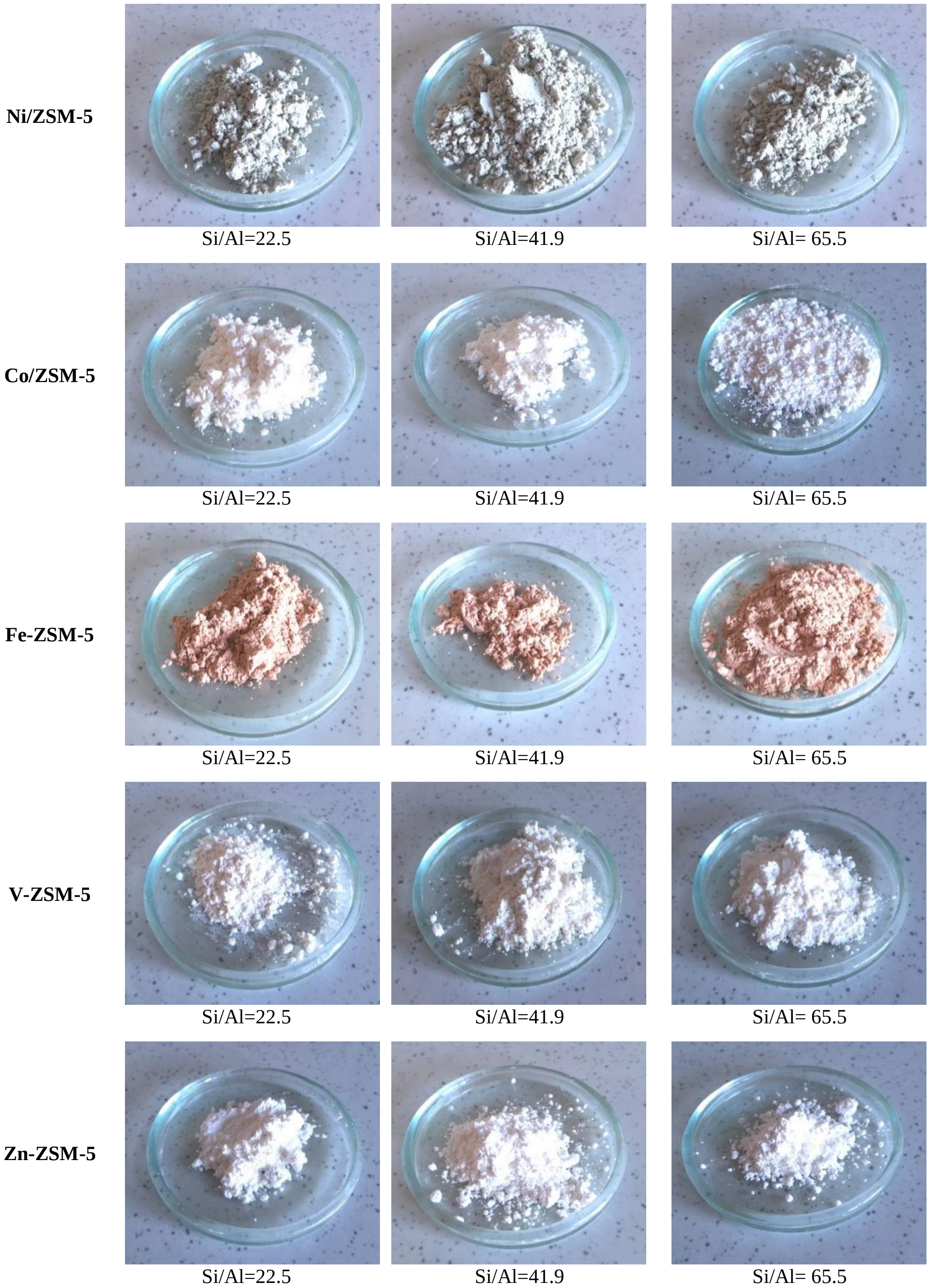


Figure 2.3
The apparence of the catalysts

The **S_{BJH}** for all used catalysts was in the range of (95 – 98 m^2/g). Ni/ZSM-5 catalyst also had the higher **S_{BET}** (382 m^2/g). Regarding to Si/Al ratio of 65.5, the average grain diameter was in the range of (16.8 – 22.5 µm). While, the surface area of the catalysts was in the range of (352 – 376 m^2/g).

2.1.2.3. Me/Ni/ZSM-5 (Ce, La, Mg, Ca and Mn) catalysts

Following the selection of the best single metal modified catalyst, it was further modified by different elements using different ratios of metals. For further investigations the Ni^{2+} was selected, and ZSM-5 catalyst with Si/Al ratio of 30 was used. The main properties of the catalysts prepared by the following procedure are summarized in **Tables 2.6-2.8** [179].

Table 2.6
The main properties of the catalysts (Me/Ni=0.1)

	Ca/Ni/ZSM-5	**Ce/Ni/ZSM-5**	**La/Ni/ZSM-5**	**Mg/Ni/ZSM-5**	**Mn/Ni/ZSM-5**
Average grain diameter, µm	0.62	0.74	0.56	0.69	0.64
S_{BET}, m^2/g	460	464	461	465	466
S_{BJH}, m^2/g	92	94	95	93	92
S_{micro}, m^2/g	318	325	320	315	322
Nickel content (on catalyst grain), %	3.89	3.83	3.86	4.12	4.10
Me content (on catalyst grain), %	0.41	0.41	0.42	0.48	0.44
Nickel content (between catalyst grains), %	4.02	3.85	3.81	4.07	4.27
Me content (between catalyst grains), %	0.40	0.39	0.42	0.46	0.44
Si/Al	30.3	30.1	30.9	32.4	29.5

Table 2.7
The main properties of the catalysts (Me/Ni=0.5)

	Ca/Ni/ZSM-5	**Ce/Ni/ZSM-5**	**La/Ni/ZSM-5**	**Mg/Ni/ZSM-5**	**Mn/Ni/ZSM-5**
Average grain diameter, µm	0.73	0.83	0.63	0.57	0.87
S_{BET}, m^2/g	419	445	408	404	395
S_{BJH}, m^2/g	93.8	92.7	90.9	89.5	92.4
S_{micro}, m^2/g	210	311	305	288	281
Nickel content (on catalyst grain), %	3.90	3.89	3.83	3.85	3.88
Me content (on catalyst grain), %	2.05	2.11	2.04	1.97	2.05
Nickel content (between catalyst grains), %	3.73	4.02	3.76	3.84	3.79
Me content (between catalyst grains), %	1.92	2.03	1.93	1.92	1.99
Si/Al	30.24	30.53	31.83	30.62	31.74

Table 2.8
The main properties of the catalysts (Me/Ni=2.0)

	Ca/Ni/ZSM-5	Ce/Ni/ZSM-5	La/Ni/ZSM-5	Mg/Ni/ZSM-5	Mn/Ni/ZSM-5
Average grain diameter, μm	1.28	1.16	0.96	1.04	0.76
S_{BET}, m^2/g	350	359	362	355	361
S_{BJH}, m^2/g	91.4	91.1	93.5	92.6	95.2
S_{micro}, m^2/g	195	280	285	257	258
Nickel content (on catalyst grain), %	3.93	3.87	3.83	3.84	3.86
Me content (on catalyst grain), %	8.51	7.70	7.72	8.38	8.03
Nickel content (between catalyst grains), %	4.05	3.67	3.52	3.82	3.77
Me content (between catalyst grains), %	8.02	7.37	7.14	7.55	7.55
Si/Al	31.48	31.07	32.35	31.17	30.36

Firstly the Ni/ZSM-5 was prepared by the before mentioned wet impregnation, then the Ni/ZSM-5 were impregnated with the second metals Me (Me=Ce, La, Mg, Ca, Mn) at three different Ni/Me ratios (0.1, 0.5, 2.0) to produce Me/Ni/ZSM-5. The dissolutions of $CeSO_4 \cdot 4H_2O$ (Reanal Kft, Hungary), $Mg(NO_3)_2$ (Sigma-Aldrich), $LaCl_3 \cdot 7H_2O$ (Reanal Kft, Hungary), $CaCl_2$ (Reanal Kft, Hungary) and $MnCl_2 \cdot 4H_2O$ (Reanal Kft, Hungary) was used for the second metal impregnation. The Ni content of the catalysts was between 3.83% and 4.12%. Three various concenteration ranges of the second metals were used: 0.41%–0.48%, 1.97%–2.11% and 7.70%–8.51%. The impregnation can affect the morphological characteristics. The increasing in metal concentrations resulted in slightly increasing of the average grain diameter of the catalysts from 0.62–0.74 to 0.76–1.28 µm. In parallel, significant reduction in the BET, BHJ and microporous surface areas was found [179]. **Figure 2.4** shows the appearance of the catalysts.

SEM method was used to investigate the morphology of the catalysts **(Figure 2.5)** [179]. As it was earlier demonstrated by the average grain size of catalysts, the micrographs clearly demonstrate that higher Me/Ni ratios led to the formation of larger catalyst agglomerates.

Ca/Ni/ZSM-5

Me/Ni=0.1 Me/Ni=0.5 Me/Ni=0.2

Ce/Ni/ZSM-5

Me/Ni=0.1 Me/Ni=0.5 Me/Ni=0.2

La/Ni/ZSM-5

Me/Ni=0.1 Me/Ni=0.5 Me/Ni=0.2

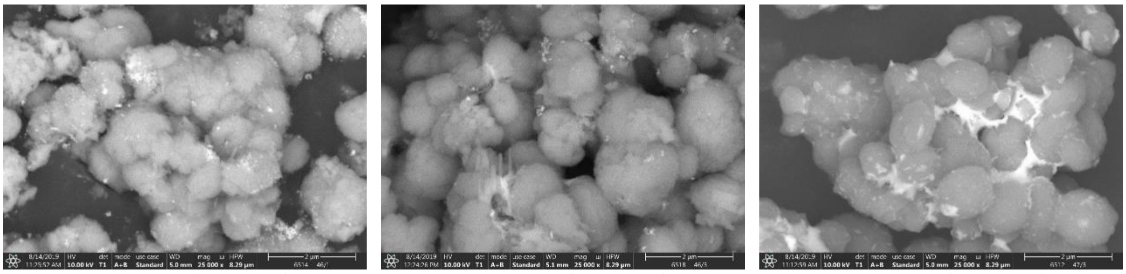
Mg/Ni/ZSM-5

Me/Ni=0.1 Me/Ni=0.5 Me/Ni=0.2

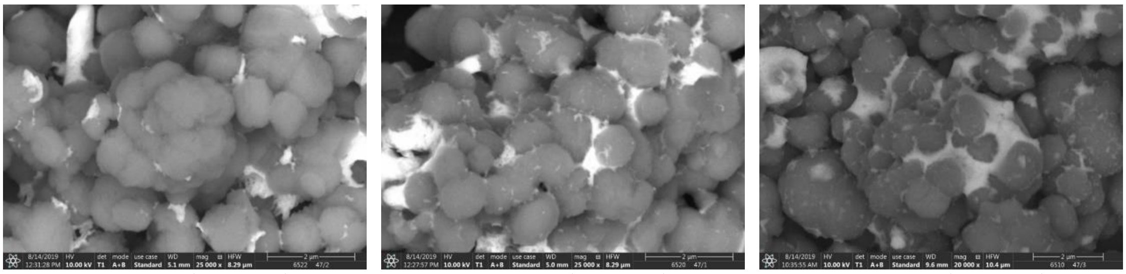
Mn/Ni/ZSM-5

Me/Ni=0.1 Me/Ni=0.5 Me/Ni=0.2

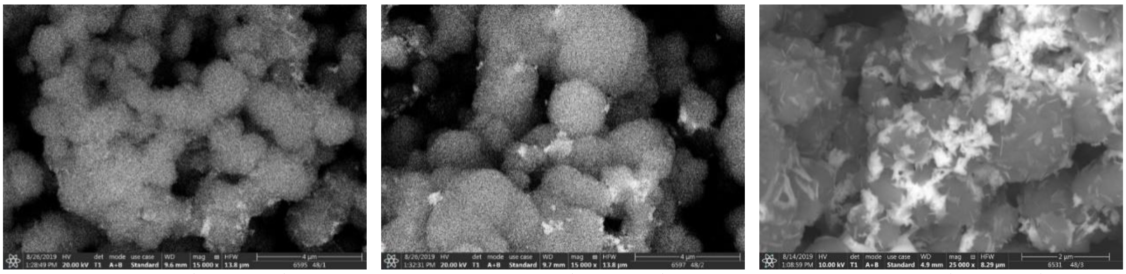
Figure 2.4
The apparence of the catalysts



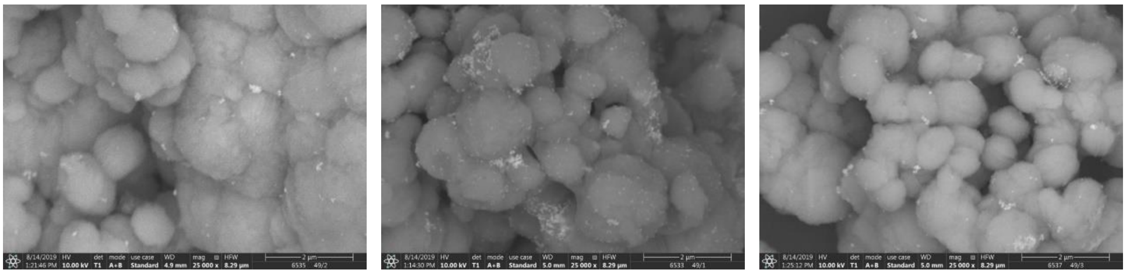
Ca/Ni/ZSM-5 (Ca/Ni=0.1) Ca/Ni/ZSM-5 (Ca/Ni=0.5) Ca/Ni/ZSM-5 (Ca/Ni=2.0)



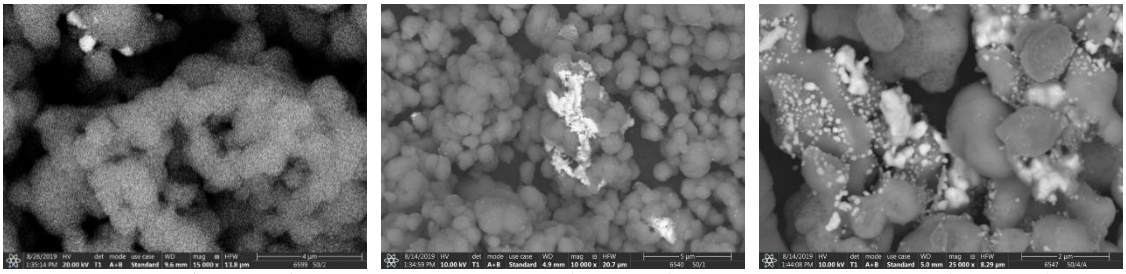
Ce/Ni/ZSM-5 (Ce/Ni=0.1) Ce/Ni/ZSM-5 (Ce/Ni=0.5) Ce/Ni/ZSM-5 (Ce/Ni=2.0)



La/Ni/ZSM-5 (La/Ni=0.1) La/Ni/ZSM-5 (La/Ni=0.5) La/Ni/ZSM-5 (La/Ni=2.0)



Mg/Ni/ZSM-5 (Mg/Ni=0.1) Mg/Ni/ZSM-5 (Mg/Ni=0.5) Mg/Ni/ZSM-5 (Mg/Ni=2.0)



Mn/Ni/ZSM-5 (Mn/Ni=0.1) Mn/Ni/ZSM-5 (Mn/Ni=0.5) Mn/Ni/ZSM-5 (Mn/Ni=2.0)

Figure 2.5
SEM micrographs of the impregnated ZSM-5 catalysts

Moreover, higher concentration of impregnating agents was found between the catalyst particles particularly at Me/Ni ratio of 2.0. On the other hand, the elemental composition of the catalyst grain corresponds to slight differences between the composition of the catalyst grain and the surface area of the majority of the catalyst particles. The elemental composition of one catalyst grain and the given surface area of the catalyst (containing grains and impregnation compounds among the catalyst grains) are reported in **Tables 2.6-2.8**. At a given concenteration, catalyst particles are not able for absorbing more ions than a certain concentration of the impregnating cation. This is also partly the reason for the aforementioned reduction in the pore surface areas, as the ions of the solution used as the impregnating agent can cover the channels of the ZSM-5 catalyst.

2.2. Processes for pyrolysis-reforming

Feedstock of raw materials were pyrolyzed in both one-stage and two-stages tubular reactor at temperature range of 550-900°C with a heating rate of 25 °C/min and nitrogen gas flow of 2.5dm^3/h. In case of both reactors, PID controller was used to set and controlled the temperature. The reaction time was 20 minutes at the set temperature (pyrolysis reactions were finished within 20 min). Volatiles from the reactor were condensed at 10°C, then a Tedlar bag was used to collect the gases product. The gases and oil products were further analysed. At the end of the expirement, the products were weighted and their yields were calculated based on the weight balance.

2.2.1. One-stage reactor

Regarding the one-stage tubular reactor temperatures of 600, 750 and 900°C were used **(Figure 2.6)**. In this case 10g of the raw material was investigated, while 10% of the catalysts were also added to the raw material in case of thermo-catalystic pyrolysis [180].

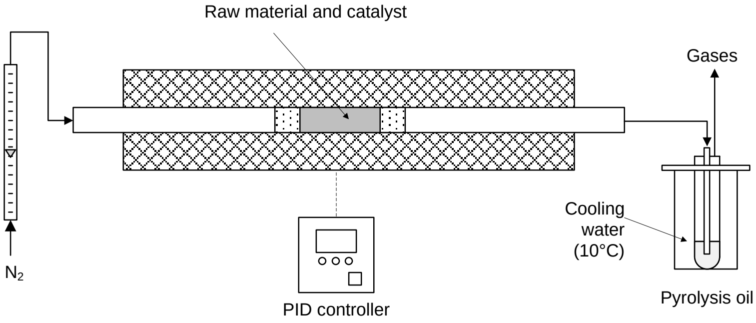


Figure 2.6
Layout of the one-stage pyrolysis process [180]

2.2.2. Two-stages reactor

In case of two-stages reactor temperatures of 550 and 850°C were used **(Figures 2.7 and 2.8)**. 5 g of raw material was placed in the first stage, while 2.5 g of catalyst was tested in the second stage separated with glass wool. Regarding the two stages reactor, not only nitrogen, but also CO_2 (dry reforming) and mixtrues of nitrogen and oxygen (partial oxidation) was used as carrier gas **(Figure 2.7)** [106, 182]. Moreover, dolomite was also used for insitu dry reforming **(Figure 2.8)** [183]. In this case 10g of dolomite was placed between the plastic sample and catalyst.

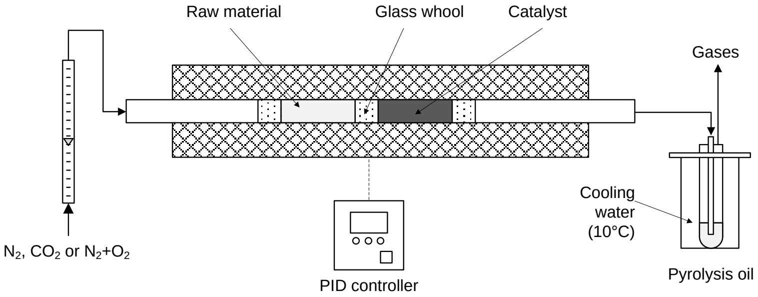


Figure 2.7
Layout of the two-stage pyrolysis process [106, 182]

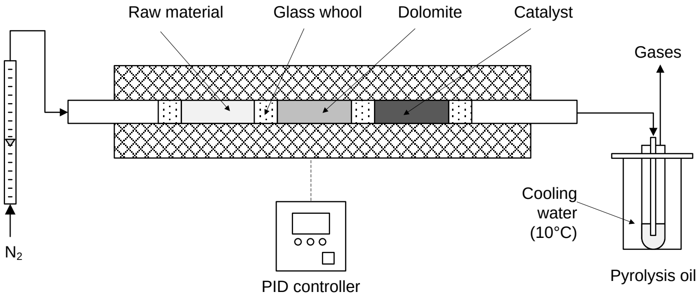


Figure 2.8
Layout of the two-stage pyrolysis process using dolomite [183]

2.3. Analytical methods

2.3.1. Gases

A GC-FID instrument (DANI GC) using isotherm conditions (T = 30 °C) was performed to analyze the hydrocarbon composition of gases. Rtx PONA (100 m × 0.25 mm, surface thickness of 0.5 μm) and Rtx-5 PONA (100 m × 0.25 mm, surface thickness of 1 μm) columns were used for the analysis.

For hydrogen, carbon monoxide and carbon dioxide analysis a GC-TCD ((Shimadzu GC-2010)) equipped Carboxen™1006 PLOT column (30 m × 0.53 mm). During the analysis, the temperature was elevated from 35 ºC (hold time 2 min) to 250 °C at 40 °C/min heating rate, with the final temperature maintained for 5 min.

2.3.2. Pyrolysis oil

A DANI GC-FID was applied for pyrolysis oil analysis. The instrument was fitted with Rtx 1 dimetil-polysiloxan capillary column (30m × 0.53 mm, thickens of 0.25 µm). Sample was dissolved in CS_2, and then injected to the instrument. The initial temperature was 40 °C for 5 min, then the temperature was elevated by 8 °C/min till 340 °C and it was kept at 340 °C till 20 min. Both the injector and detector temperature were 340 °C.

2.3.3. Thermogravimetric analysis

The efficiency of selected catalysts in pyrolysis was analyzed by thermogravimetric analysis (Shimadzu DTG-60 instrument with TA-60WS thermal analyser). The analysis was performed at Xi’an Jiaotogn University, Xi’an, China. Samples were mixed with catalysts and heated by 20 °C/min till 750 °C. The sample amount was 5-15 mg. The flow rate of nitrogen carrier gas was 75 ml/min [114].

2.3.4. Temperature Programed Oxydation

Carbon deposition on catalyst was analysed by temperature programmed oxidation. 250 mg of the catalysts were heated in air using thermogravimetric method by 10 °C/min heating rate (MOM DERIVATOGRAPH Q-1500 D type instrument).

2.3.5. Transmison Electron Microscopy

The CNT on catalyst surface was analysed at the Nanolab, University of Pannonia. Samples were prepared by depositing a drop of aqueous suspension of sediment particles on copper TEM grids covered by an ultrathin amorphous carbon film. The analyses were performed using a Talos F200X G2 instrument (Thermo Fisher), operated at 200 kV accelerating voltage, equipped with a field-emission gun and a four-detector Super-X energy-dispersive X-ray spectrometer.

2.4. Research plan

Figure 2.9 summarizes the research plan. Firstly, a literature survey was done to figure out the main finding of the previous works in terms of feedstock types and syngas yields. Then raw materilas with catalysts were selected and characterized.

Figure 2.9
The research plan

Different active metals with different supports and different Si/Al ratios were prepared and further characterized for better understanding of catalysts behaviors. The catalysts then investigated for the decomposition of waste plastic at various reaction temperatures. Based on the obtained results, the best catalyst with best support was chosen for further investigation. Additionally, TG-FTIR was used to the analysis of raw materials in order to determine the main reaction kinetic parameters.

After that, the catalysts were further modified with various second metals of promoters. The new modified catalysts were tested for the pyrolysis-gasification of waste plastic in the presence of various reaction atmospheres (nitrogen, oxygen and carbon dioxide). Oxygen atmosphere was used to enhance the partial oxidation reaction, while carbon dioxde was used to promote the dry reforming reaction. Moreover, dolomite was used for insitu dry reforming. The influence of different atmosphere type on the syngas production was studied. The obtained results from the different expirements were analyzed and evaluated. At the end and based on the obtained data, the main finding were highlighted in the conclusion part.

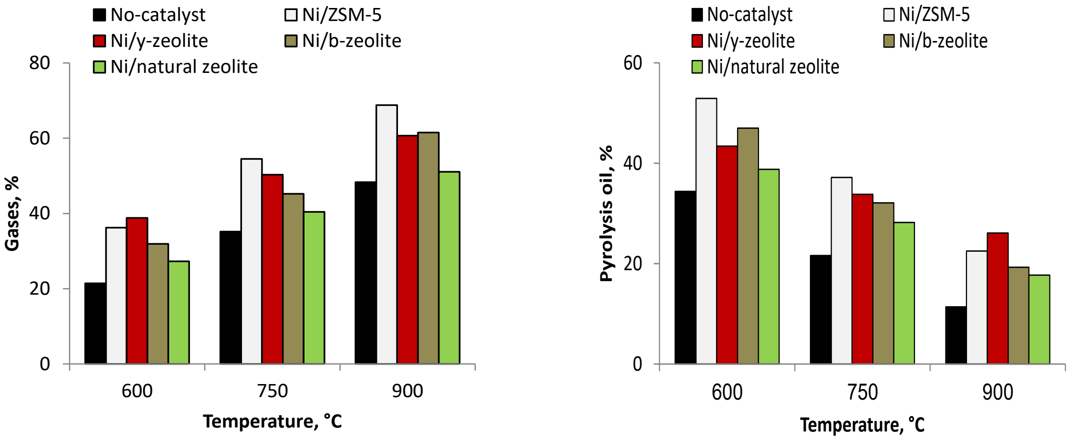
3. RESULTS AND DISCUSSION

3.1. Investigation of the effect of catalyst supporters and temperatures

In this chapter different zeolites as catalyst supporters were loaded by Ni, then their effects to the high temperature pyrolysis reactions were investigated in a one stage reactor at 600, 750 and 900 °C.

3.1.1. Product yields

Figure 3.1 (a,b) illustrates the yields of gases and pyrolysis oil from the decomposition reactions. The obtained data shows that the presence of catalysts resulted in more yields of both gases and pyrolysis oil in comparison to the non-catalytic process. Pyrolysis consumes a lot of energy which can be minimized by the presence of catalysts. More gas was found at higher pyrolysis temperature. The maximum gas product was obtained in the presence of Ni/ZSM-5 catalyst. Based on the reaction temperature, the yield of gas was increased over Ni/ZSM-5 catalyst with 43-69%, while the natural zeolite supported Ni modified catalysts had the less effect to the decomposition reactions (6-28% increasing).



a) b)

Figure 3.1 (a,b)
The yields of products (a) gases, (b) pyrolysis oil

The catalysts efficiency had the order of Ni/Natural zeolite<Ni/β-zeolite<Ni/ZSM-5<Ni/y-zeolite at 600°C, and Ni/Natural zeolite<Ni/y-zeolite<Ni/β-zeolite<Ni/ZSM-5 at 900°C. The order can be attributed to the difference in surface areas of the catalysts.

The pyrolysis oil yields for the non-catalytic process were 34.4, 21.6 and 11.4 % at 600, 750 and 900 °C, respectively (**Figure 3.1 (b))**. By introducing the catalyst to the process, the maximum yield of pyrolysis oil was obtained at 600 °C in the presence of Ni/ZSM-5 (52.9 %). β-zeolite showed also a good performance in pyrolysis reactions resulted pyrolysis oils, however its activity rapidly decreased with increasing temperature. Ni/y-zeolite catalyst had the slowest decreasing tendency. Hence, higher temperature promoted and favours the deeper cracking of primary decomposition products.

3.1.2. Gases

The influence of catalyst type and reaction temperature on the gas compositions are shown in **Figure 3.2**. Regardless of the catalyst impact, the GC-results showed that higher temperature promoted the production of hydrogen (14.1 % at 900 °C). This is due to the more cracking of hydrocarbons at high pyrolysis temperature as the following reaction.

$$C_nH_m \rightarrow C_kH_l + C + 2H_2 \quad (3.1)$$

Moreover, the reactions of intramolecular hydrogen transfer are favoured at elevated temperatures which explain the increasing of branched hydrocarbons (C_2-C_5) in the gas yields at 900°C. Regarding to the other compositions, gases contain CO and CO_2 due to the presence of PET in the feedstock. The results showed that CO_2 concenteration was higher than CO especially at high temperature. This phenomenon was the consequence of PET structure, in-situ water-gas shift reaction and steam reforming of methane *(3.2-3.4)*. While, the water-gas reaction was behained CO in the product. In general, higher temperature increased the rate of Boudouard reaction which resulted in more ratio of CO_2/CO *(3.5)*.

$$CO + H_2O \rightarrow CO_2 + 2H_2 \quad (3.2)$$

$$CH_4 + H_2O \rightarrow CO_2 + 2H_2 \quad (3.3)$$

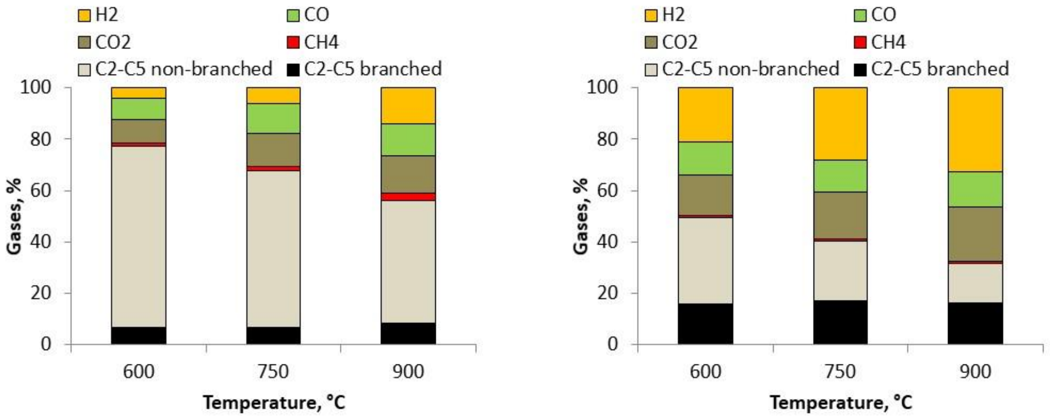
$$C + H_2O \rightarrow CO + 2H_2 \quad (3.4)$$

$$CO_2 + C \rightarrow CO \quad (3.5)$$

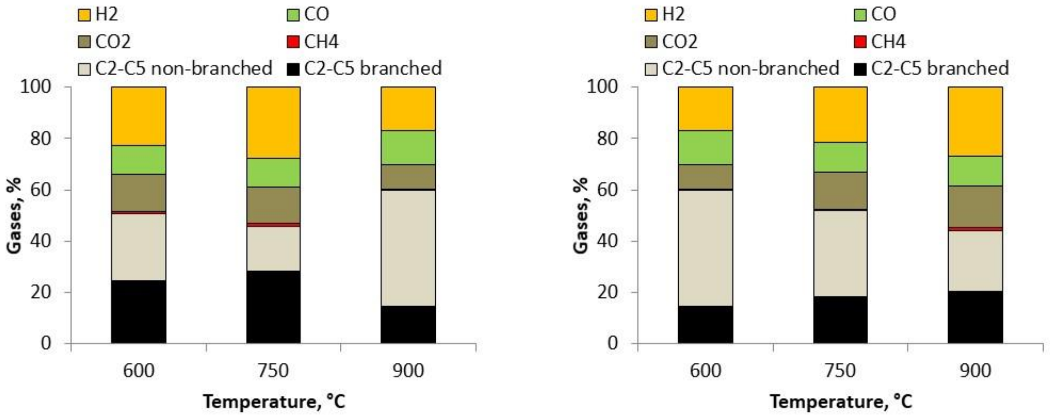
Slightly change in the concentration of methane (1.6 - 2.9 %) was reported with temperature due to the methanization reaction *(3.6)*.

$$C + 2H_2 \rightarrow CH_4 \quad (3.6)$$

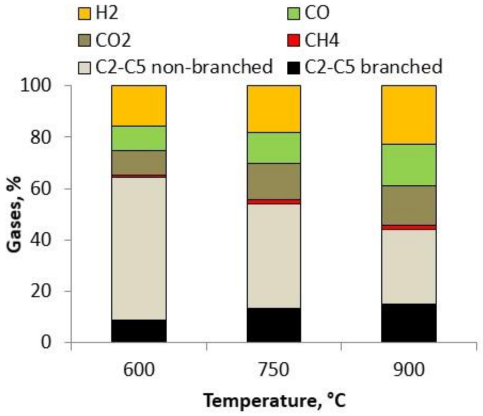
Hydrogen and other hydrocarbons are also affected by the presence of catalysts. Acidic zeolite catalysts promoted the formation of hydrogen, CO, CO_2 and light hydrocarbons due to their activity for increasing the decomposition rate of raw materials. The maxiumum H_2 yield for catalytic process was obtained with Ni/ZSM-5 catalyst (32.6 %).



No-catalyst Ni/ZSM-5



Ni/y-zeolite Ni/b-zeolite



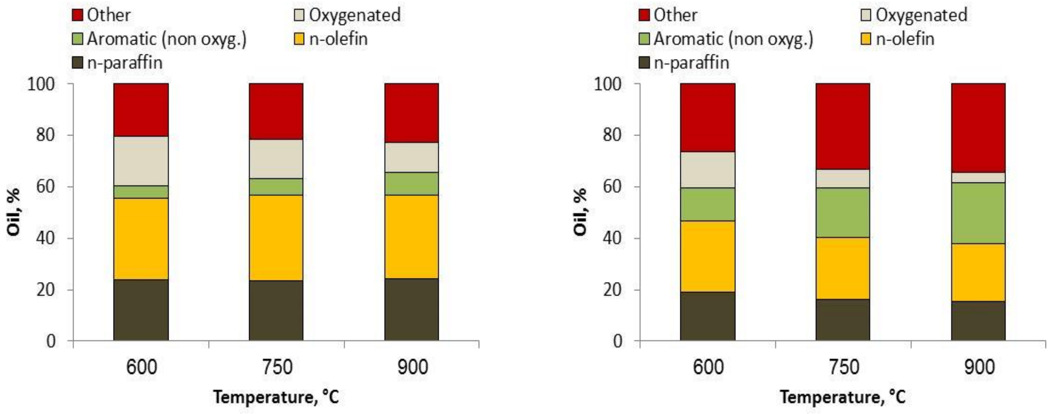
Natural zeolite

Figure 3.2
The composition of gases

The influence of zeolite catalyst type on hydrogen yield from waste plastic was also studied by Yao et al. [52]. The authors observed that ZSM-5 catalyst generated higher yield of H_2 and CO in comparison to other types of zeolites (b-zeolite and Y- zeolite). Their obtained data showed that H_2 and CO yields were 55 vol% and 30 vol%, respectively. Regarding to branched hydrocarbons, introducing the catalysts resulted in more intermolecular hydrogen transfer and isomerization reactions which explain the increasing over Ni/y-zeolite catalyst (28.1 % at 900 °C). While opposite trend was reported for the non-branched hydrocarbons. However, the less influence in branching reactions was reported over Ni modified by natural zeolite as it can produces only 15.2 % at 900 °C.

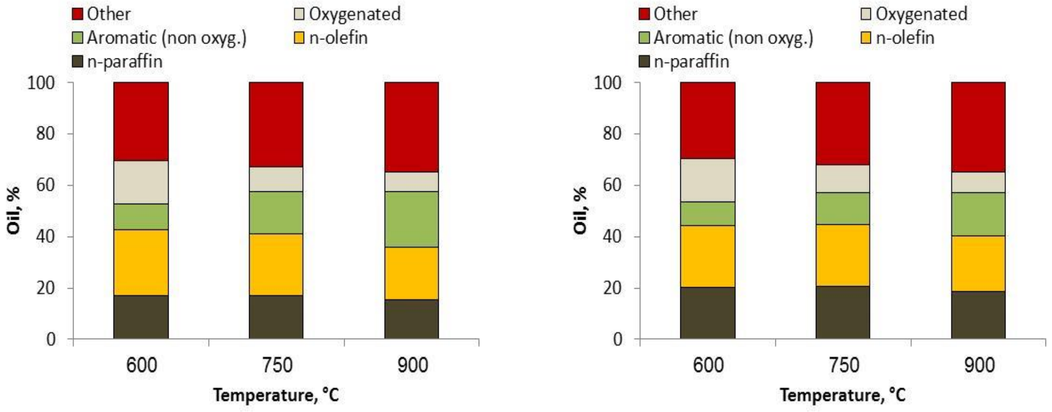
3.1.3. Pyrolysis oil

The effects of reaction temperature and catalyst type on the pyrolysis oil are shown in **Figure 3.3**.



No-catalyst

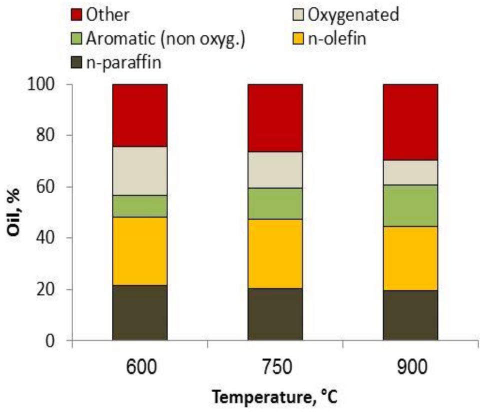
Ni/ZSM-5



Ni/y-zeolite

Ni/b-zeolite

Figure 3.3
The composition of pyrolysis oil



Natural zeolite

Figure 3.3
The composition of pyrolysis oil (cont.)

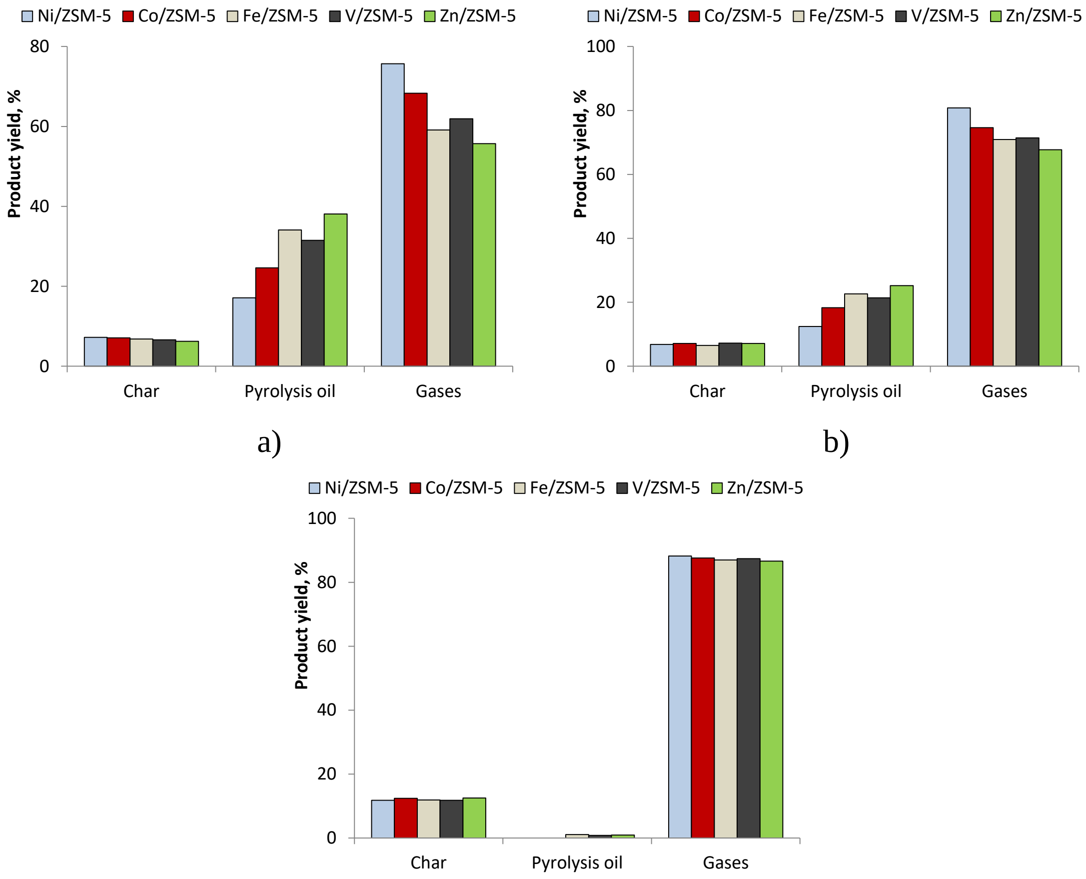
The results demonstrate that temperature has not affected the concentration of n-olefins and n-paraffin significantly, while, introducing the catalysts resulted in decreasing of their concentration (31.9-33.3 % to 20.2-27.0 % in case of n-olefins) and (23.3-24.3 % to 15.4-21.7 % in case of n-paraffins), respectively. Temperature also has visible effect on the concentration of non-oxygenated aromatics as it is increased with rising the temperature. The increasing in aromatic compunds was the consequnce of side broken reactions of phenol derivates and aromatization reactions as well. However, the maximum aromatic yield was achieved over Ni/ZSM-5 catalyst (23.7 %).

In addition to n-olefins, n-paraffins and non-oxygenated aromatics, oil contained branched and oxygenated compounds. Increasing of temperature had positive influnce on the branched compounds, while opposite effect was reported for the oxygenated compounds. For the catalytic pyrolysis, Ni/y-zeolite and Ni/ β-zeolite catalysts produced the highest yield of branched compounds (35 % at 900 °C). Higher pyrolysis temperature and acidic properties of the catalyst are favoured for the isomerization reactions.

3.2. Investigation of the effect of metal

3.2.1. Product yields

The investigation of the influence of different catalysts with different Si/Al ratio and metal content was carried out at 700 °C. The yields of products are summarized in **Figure 3.4(a,b,c)**. The results well demonstrates that high yield of gases was found in comparison to other product yields. Furthermore, the same trend was reported by increasing the Si/Al ratio for the used catalysts. Gasification was behind that phenomena as the oil yield was only 1.1 %. Moreover, as it is well known the carbenium ions formed in the initiation reaction step are resposible for the broken of C-C bonds of polymer molecules. The formation of these ions is favoued at the catalysts with higher Si/Al ratio. However, the too high of Si/Al content may lead to to very quick deactivation of the catalyst due to the blockage of catalyst pore mouth.



a) b)

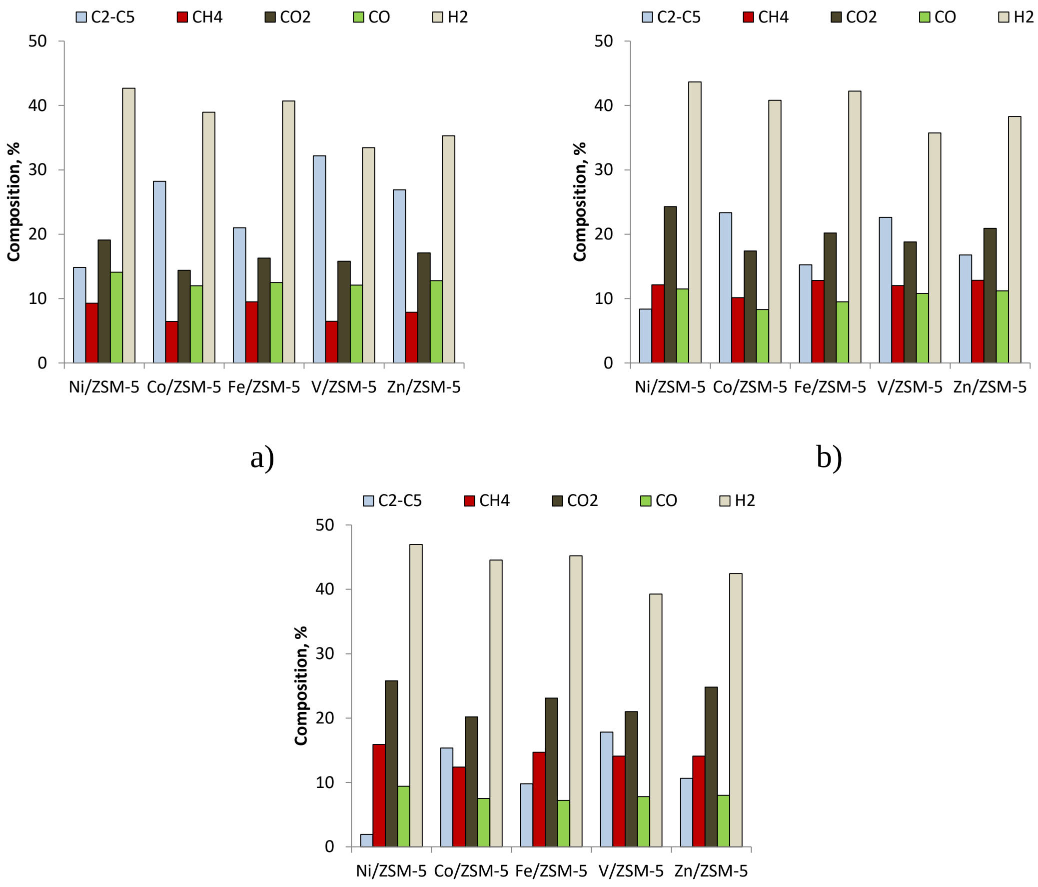
c)

Figure 3.4 (a,b,c)
Product yield using Me/ZSM-5 catalysts with
different Si/Al ratios (a= 22.5, b= 41.9, c= 65.5)

Comparing the gas yield over the catalysts, Ni/ZSM-5 produced the highest amount of gases for the various Si/Al ratios due to the ability of Ni catalyst for speed up the reaction rate and resulted in lighter compounds (gases). In contrast, the lowest gas yield was reported with Zn/ZSM-5 catalyst as it is produced 55.7 %, 67.7 % and 86.6 % of gas product for the Si/Al ratio of 22.5, 41.9 and 65.5, respectively. While, the maximum oil product (38.1 %) was repoted over Zn/ZSM-5 catalyst with 22.5 of Si/Al ratio. Regarding the char yield, the Boudoard reaction (2CO → CO_2 + C) was the reason for the maxium yield at Si/Al ratio of 65.5 in the presence on Zn/ZSM-5 catalyst. However, no significant change in the char yield was found over the different catalyst with the same Si/Al ratio.

3.2.2. Gases

The influence of catalyst type and Si/Al ratio on the decomposition reaction and compositions of gases are shown in **Figure 3.5(a,b,c)**.



a) b)

c)

Figure 3.5(a,b,c)
The composition of gases using Me/ZSM-5 catalysts with
different Si/Al ratio (a= 22.5, b= 41.9, c= 65.5)

Hydrogen, carbon monoxide, carbon dioxide, methane, branched and non-branched hydrocarbons (up to C_5) were the main compositions of gas product. Based on the obtained results, the hydrogen content was slightly influenced by the Si/Al ratio of catalyst. Among the different used catalysts in the expirements, the results observed that the highest yields of hydrogen were achieved over Ni/ZSM-5 catalyst for any Si/Al ratios which were 42.7%, 43.7% and 47.0 %. While, V/ZSM-5 catalyst produced the lower yields of hydrogen, which were 33.4 %, 35.8 % and 39.3 % for Si/Al of 22.5, 41.9 and 65.5, respectively. CO and CO_2 in gases product were mainly the consequnce of the decomposition reaction for the polyethylene terephthalate in the raw materials. Generally, the concentration of CO_2 was higher than CO which can be attributed to the in-situ water-gas shift reaction. However, higher concentration of CO_2 was reported with increasing the Si/Al ratio compared to CO concenteration. Regarding to methane concentration in the gas products, Si/Al ratio had slightly effect on the methane yield. The maximum concenteration of methane (17.1 %) was obtained with higher Si/Al ratio over Ni/ZSM-5 catalyst. This behavior corresponds to the high activity of this catalyst in C-C scission.

Regarding to other hydrocarbons in the gas yield, dominate presence of ethane and ethene was found. On the other hand, the concentrations of saturated hydrocarbons were always lower, than the unsaturated for all used catalysts. However, V/ZSM-5 catalyst with Si/Al ratio of 22.5 produced the highest yield of non-branched hydrocarbons, while the Co/ZSM-5 catalyst with Si/Al ratio of 65.5 had the lowest yield. However, advanced property was reported for the Co^{2+}, Fe^{2+} and Zn^{2+} especially in isomerization effect. The ratio of branched and non-branched hydrocarbons in gases using Me/ZSM-5 catalysts with different Si/Al ratio is summarized in **Figure 3.6**.

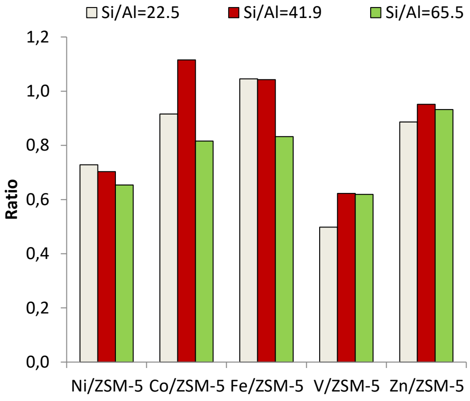
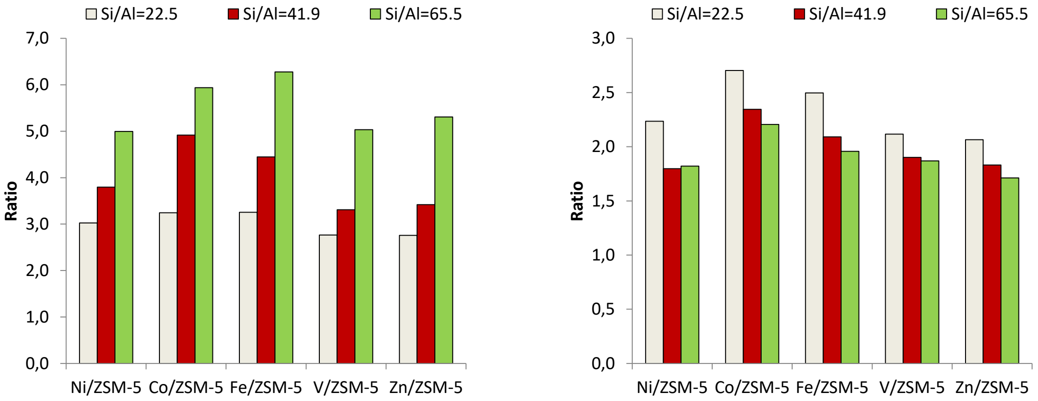


Figure 3.6
The ratio of branched and non-branched hydrocarbons in gases using Me/ZSM-5 catalysts with different Si/Al ratio

The results showed that the Si/Al ratios have visible effect on the ratio of branched/non-branced hydrocarbons as it is increased with 41.9 Si/Al ratio then decreased with higher ratio of Si/Al ratio of 65.5 in most cases. However, the maximum ratio of branched/non-branced hydrocarbons (1.1 %) was obtained in the presence of Co/ZSM-5 catalyst at Si/Al ratio of 41.9. While the minimum ratio (0.49 %) was reported over V catalyst at 22.5 Si/Al ratio. As it is before mentioned, the acivity of Co catalyst in isomerization effect was behind that increasing.

The ratios of H_2/CO and H_2/CO_2 in gases using Me/ZSM-5 catalysts with different Si/Al ratio are shown in **Figure 3.7**. Based on the obtained data, increasing of Si/Al ratio led to increasing of H_2/CO ratio for all catalyst type. The maximum H_2/CO value (6.3 %) was obtained in the presence of Fe/ZSM-5 catalyst at 65.5 of Si/Al ratio. On the other hand, the ratio of H_2/CO_2 in the gases was decreased by increasing the Si/Al ratio. The maximum H_2/CO_2 ratio (2.7 %) was reported over Co/ZSM-5 catalyst at 22.5 Si/Al ratio.



Ratio of H_2/CO

Ratio of H_2/CO_2

Figure 3.7
The ratio of H_2/CO and H_2/CO_2 in gases using Me/ZSM-5 catalysts with different Si/Al ratio

Figure 3.8 summarizes the yields of hydrogen and carbon-monoxide using Me/ZSM-5 catalysts with different Si/Al ratio. Data showed that visible influenced of the Si/Al ratio on the H_2 and CO yields were found over the various used catalysts. Increasing the Si/Al content of the catalysts resulted in clear increasing of H_2 and ratio of 65.5 produced the most H_2 (82.9 mmol/g). Hence, increasing the silica content of the catalyst had positive effect on the syngas production due to the more hydrogen transfer reaction. Dingding et al. [52] also investigated the influence of Si/Al ratios of zeolite support for the hydrogen and syngas production from waste polyethylene. The authors performed different Si/Al ratios from 30 to 80. Their obtained data showed that Ni/ZSM-5 catalyst with Si/Al ratio of 80 generated 91.54 mmol/g of syngas.

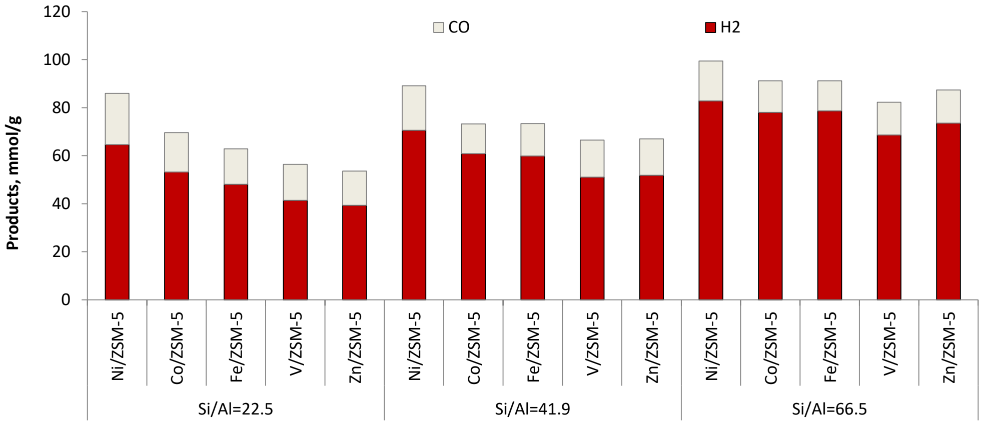
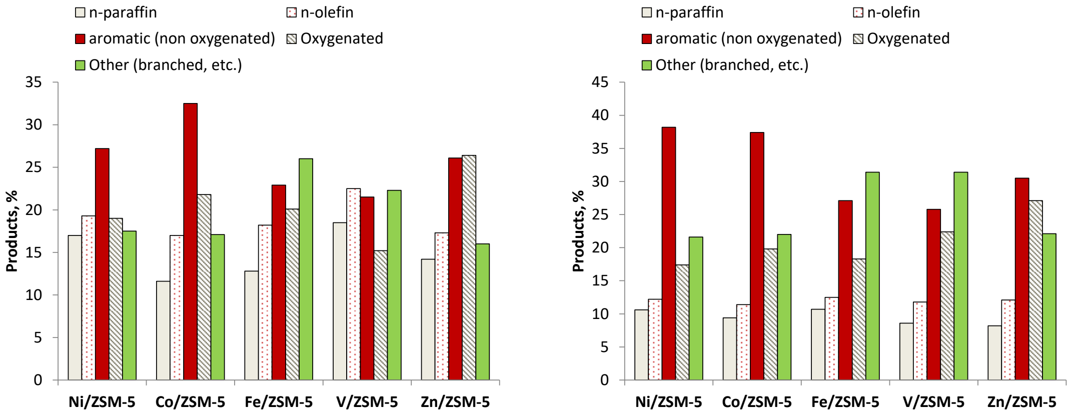


Figure 3.8
The yields of hydrogen and carbon-monoxide using Me/ZSM-5 catalysts with different Si/Al ratio

However, among the various used catalysts, Ni/ZSM-5 produced the highest yield of syngas (99.4 mmol/g) which was attributed to the high surface area as confirmed by BET results. Furthermore, the Ni has the ability to increase the conversion rate compared to other active metals. In contrast, slightly decreasing of CO yield was reported with increasing the alumina content of the catalyst. However, the maximum CO product (21.3 mmol/g) was achieved at lower Si/Al ratio (22.5) over Ni/ZSM-5 catalyst.

3.2.3. Pyrolysis oil

The compositions of pyrolysis oil are shown in **Figure 3.9(a,b).** According to results pyrolysis oil product contained normal-olefins, normal-paraffin, non-oxygenated aromatics, branched and oxygenated compounds. Different transition metals and different Si/Al ratio of the ZSM-5 support have visible effect on the concentration of n-paraffin, n-olefin, aromatics, and branched hydrocarbons. While, the concenteration of n-saturated and unsaturated compounds not influenced by the ratio of Si/Al. For both Si/Al ratio of 22.5 and 49.1, the ratio of n-saturated and unsaturated compounds was in the range of 0.68-0.88 %. However, using Ni supported by ZSM-5 catalyst with Si/Al ratio of 22.5 resulted in 17.0 % of n-paraffin concenteration, while, the concentration of n-paraffin was 10.0 % over 49.1 of Si/Al ratio. In general, lower concentration of n-paraffin and n-olefin compounds were observed over the catalysts with higher Si/Al ratio which explain the higher yields of aromatic and other hydrocarbons. The presence of ZSM-5 catalyst with higher Si/Al ratio promoted the aromatization reaction and cracking effiency of heavy compunds which led to more aromatic in the oil yield.



a)   b)

Figure 3.9(a,b)
The composition of pyrolysis oil using Me/ZSM-5 catalysts with different Si/Al ratio (a= 22.5, b= 41.9)

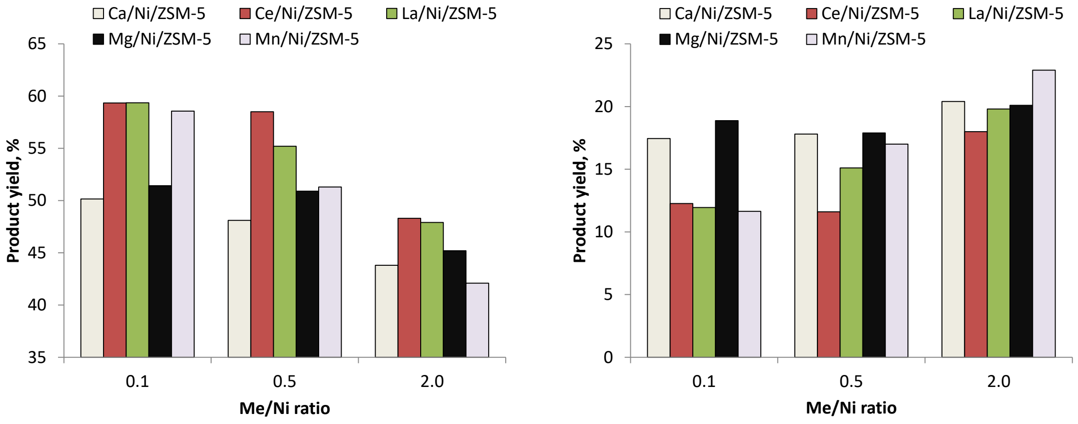
The active sites of zeolite catalyst can converts the light hydrocarbons into aromatic compounds which is agree with the results obtained in the literature [184]. However, the maximum aromatic compounds (38.2 %) were achieved over Ni/ZSM-5 catalyst, while Fe/ZSM-5 catalyst produced the highest yield of branced hydrocarbons (31.4 %).

3.3. Investigation of the second metal/catalyst ratio

Based on earlier demonstrated results, the ZSM-5 catalyst supporter and Ni as base transition metal was choosen for further investigation. Then different Me/Ni/ZSM-5 catalysts were synthetized by wet impregnation method (see in Section 2.1.2.3).

3.3.1. Product yields

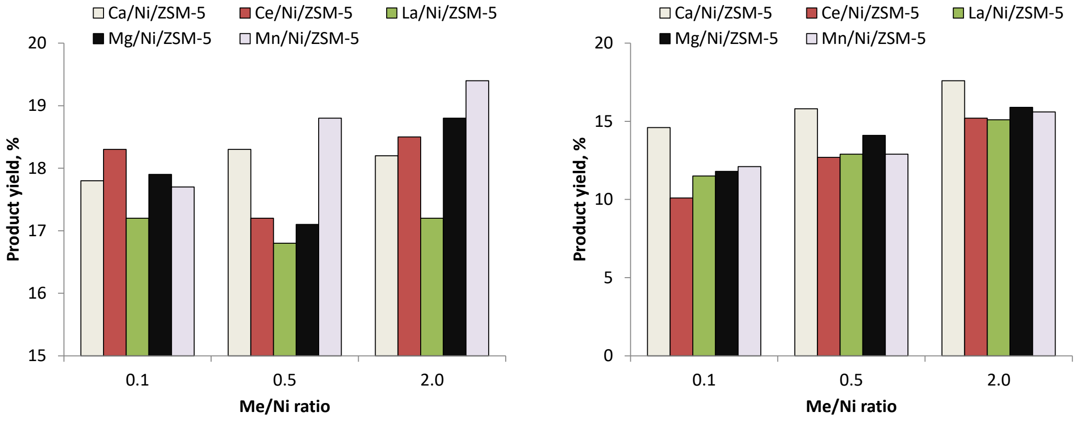
Figure 3.10 illustrates the product yields from the catalytic pyrolysis of waste plastics mixture with different Me/Ni ratio (0.1, 0.5 and 2.0) at 700 °C. Based on the obtained results, dominate formation of gases were found in comparison to other pyrolysis products, which was attributed to the high reaction temperature which led to more gasification reactions. Results demonstrated that increasing of second metal content has reverse impact on the gas yield as it is decreased. Me/Ni ratio of 0.1 produced the maximum gas yield compared to other two ratio (0.5 and 2.0). The highest yields were observed by the addition of Ce, La and Mn catalysts which were 59.3%, 59.4% and 58.6% respectively.



Gases

Pyrolysis oil

Figure 3.10
Product yields using different Me/Ni ratio



Char

Carbon deposition

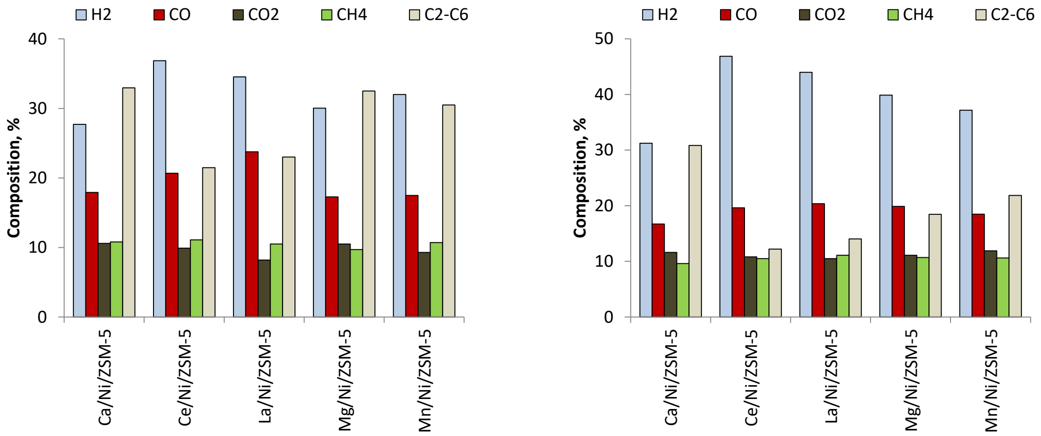
Figure 3.10
Product yields using different Me/Ni ratio (cont.)

Regarding to pyrolysis oil product, the addition of second metal has positive effect on their yields. The maximum amount of oil yield was obtained at the highest ratio of Me/Ni ratio, which was 22.9 % over Mn catalyst. Similar trend was reported for the char yield and carbon deposition on catalyst surface with increasing the concentration of second metals. The maximum carbon deposition (17.6 %) was reported over Ca catalyst at Me/Ni ratio of 2.0. These reasons were behind the decreasing of gas product at 2.0 of Me/Ni ratio.

3.3.2. Gases

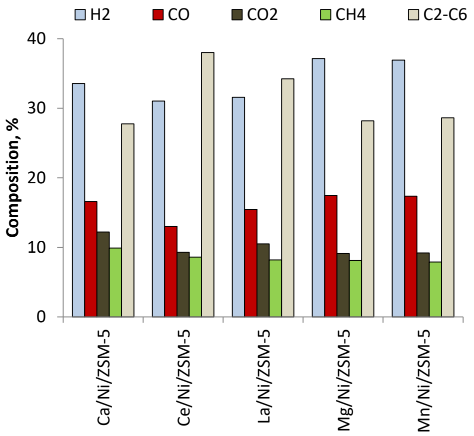
The influence of catalyst type and different Me/Ni ratio on the gas compositions are shown in **Figure 3.11(a,b,c)**. Among the different used catalysts, Ce showed the highest efficiency in terms of hydrogen production especially at 0.5 of Me/Ni ratio which was

49.2 %. This was attributed to the synergistic effects of Ce and Ni. However, increasing of second promoters to 2.0 resulted in decreasing of both hydrogen and carbon monoxide yields. On the other hand, the minimum hydrogen yield (27.7 %) was achieved over Ca catalyst at lower ratio of Me/Ni.



a) b)

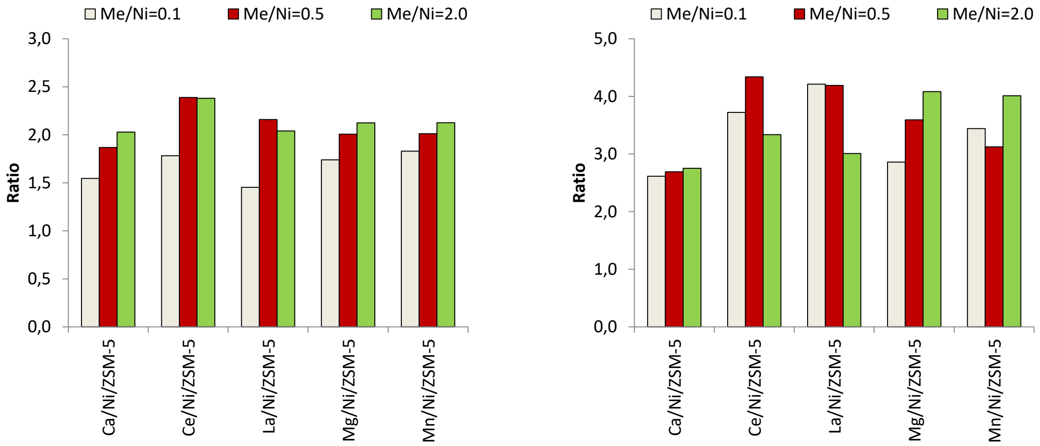
Figure 3.11
The composition of gases using Me/Ni/ZSM-5 catalysts with different Me/Ni ratio



c)

Figure 3.11(a,b,c)
The composition of gases using Me/Ni/ZSM-5 catalysts with different Me/Ni ratio (a= 0.1, b= 0.5, c= 2.0)(cont.)

No significant effect was reported on the concntration of methane product by changing the catalyst type and Me/Ni ratio from 0.1 to 0.5. In contrast, slightly decreasing was found with 2.0 Me/Ni ratio. Regarding to other gas compositions, visible effect was reported on the C_2-C_6 hydrocarbons by the addition of the promoters. The ratio of H_2/CO and H_2/CO_2 in gases using different Me/ZSM-5 catalysts with different Me content are shown in **Figure 3.12(a,b)**.



a) b)

Figure 3.12(a,b)
The ratio of H_2/CO and H_2/CO_2 in gases using Me/Ni/ZSM-5 catalysts with different Me/Ni ratio
(a= ratio of H_2/CO, b= ratio of H_2/CO_2)

Slight changes were reported in the ratio of H_2/CO and H_2/CO_2 ratios with changing the second metal promoters. Increasing of metal content from 0.1 to 0.5 led to increasing of H_2/CO ratio for all catalysts type. While, no significant changes were found in the ratio of H_2/CO by increasing the second metal content from 0.5 to 2.0. However, the maximum H_2/CO ratio was found in the presence of Ce/Ni/ZSM-5 catalyst at Me of 0.5 and 2.0 which was 2.4 %. On the other hand, the ratio H_2/CO_2 was increased by increasing the concentration of second metal to 0.5 and then decreased with higher metal content of 2.0 using Ce/Ni/ZSM-5 catalyst. Comparing the used catalysts, the maximum H_2/CO_2 ratio (4.3 %) was found in the presence of Ce/Ni/ZSM-5 catalyst at Me content of 0.5.

Figure 3.13 summarizes the yields of hydrogen and carbon-monoxide using Me/ZSM-5 catalysts with different Me ratio. Different trends were found in the H_2 and CO yields with changing the concentration of second metal and metal type. First, the amount of H_2 was increased with increasing the Me concentration, but further increasing of Me content to 2.0 resulted in decreasing of H_2 yield. Ce/Ni/ZSM-5 and La/Ni/ZSM-5 catalysts produced the maximum H_2 product at 0.5 of Me/Ni with an amount of 54.8 and 48.6 mmol/g, respectively. In another work, Nahil et al. [61] investigated the influence of a range of metals addition (Mn, Mg, Ce, Zn, Ca) to Ni-based catalysts at Ni:Me molar ratio of (1:1) for the hydrogen production from waste polyprpylene. Their obtained data showed that Ce metal promoter produced a 63.1 mmol/g of hydrogen. However, the the synergistic effects of cerium, lanthanum and nickel can also be blamed for the increasing of hydrogen production.

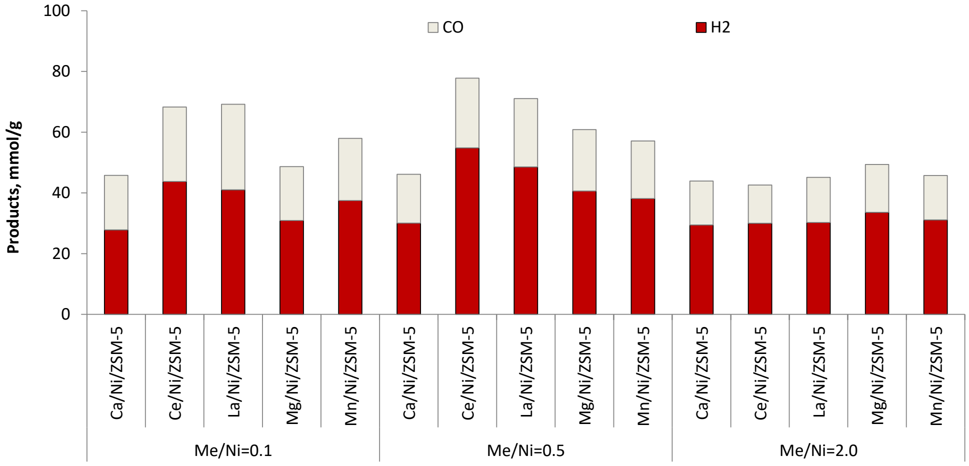


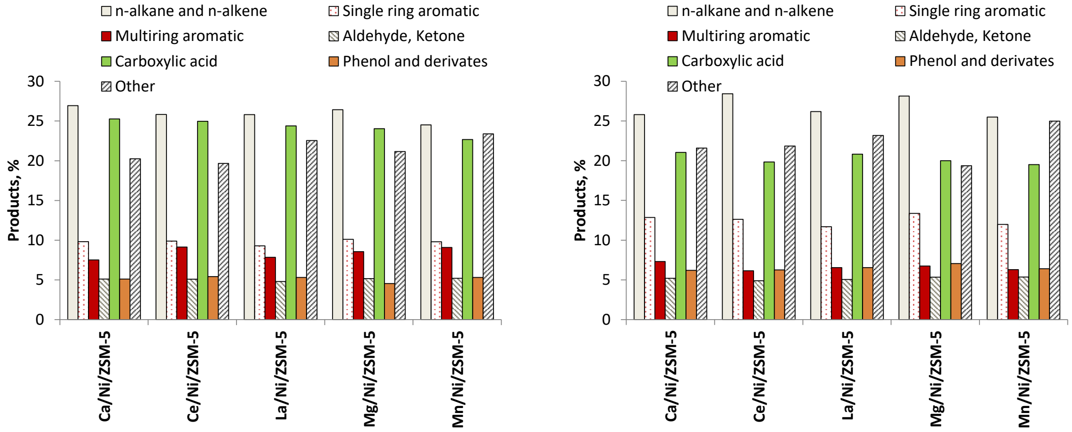
Figure 3.13

The yields of hydrogen and carbon-monoxide using Me/Ni/ZSM-5 catalysts with different Me/Ni ratio

In contrast, the lowest yield of hydrogen (27.8 mmol/g) was obtained at 0.1 of metal/catalyst ratio in the presence of Ca/Ni/ZSM-5 catalyst. Regarding to the CO in the product, the yield was decreased with changing the Me content from 0.5 to 2.0. However, the maximum CO yield (28.2 mmol/g) was obtained at ratio of 0.5 over La/Ni/ZSM-5 catalyst.

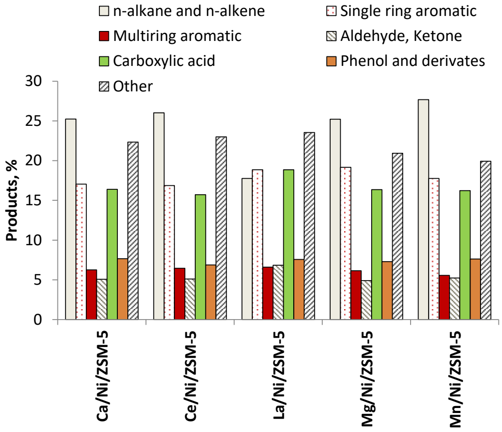
3.3.3. Pyrolysis oil

Based on the data, n-alkanes, n-alkenes, oxygenated, single and multi-aromatic rings compounds were the main compositions in pyrolysis oil as shown in **Figure 3.14**. The oxygen-containing hydrocarbons were in the form of aldehydes, ketones, alcohols, carboxylic acids and phenol type compounds. In one hand, the presence of aromatic compounds in the pyrolysis oil was attributed to the PET content in the raw material. On the other hand, the cyclization and aromatization reactions over synthetic zeolite should also be attributed for hight aromatic content. Oxygenated compounds are found in the form of phenol, carboxylic acids, ketones, alcohols and aldehydes. Results demonstrated that 24.5-28.4 % of n-alkanes and n-alkenes were found in the oil product. However, the increasing of second metal content in the catalyst has negligible influence on the concentration of n-alkanes and n-alkenes. While visible decreasing from 35.5 % to 27.7 % was reported over the concentration of oxygenated compounds with increasing of metal content. Also, same trend was observed for the multi ring aromatic as it is decreased from 7.5-9.1% to 5.6-6.1% with the addition of second promoters. While, the obtained results showed that increasing of second metal content had positive influence on the concentration of single ring aromatic.



Me/Ni=0.1

Me/Ni=0.5



Me/Ni=2.0

Figure 3.14
The composition of pyrolysis oil using Me/Ni/ZSM-5 catalysts with different Me/Ni ratio

3.4. Reaction kinetic parameters by TG analysis of raw materials

Based on the earlier demonstrated results, ZSM-5 based catalysts with 0.5 Me:Ni elemental ratio was selected for further investigation. Firstly the apparent kinetic parameters of the thermo-catalytic pyrolysis reactions were calculated by first order kinetic approach based on the equations (3.7) and (3.8). In this chapter the effects of Ni/ZSM-5 and different Me/Ni/ZSM-5 catalysts (Me=Ca, Ce, La, Mg, Mn) were investigated [114].

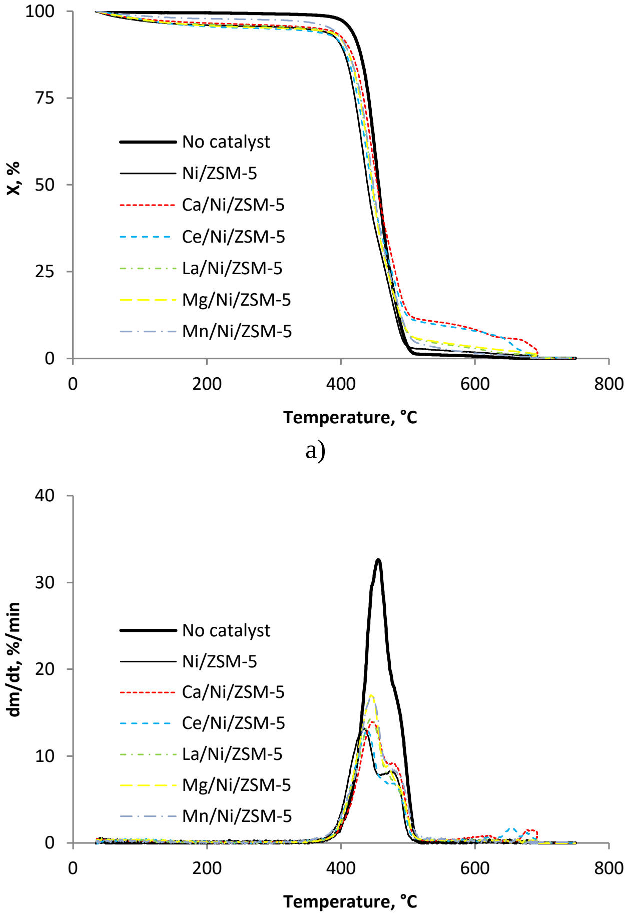
$$x = \frac{m_i - m_t}{m_i - m_f} \cdot 100 \tag{3.7}$$

$$\frac{dx}{dt} = A \cdot e^{\left(-\frac{E_a}{RT}\right)(1-x)} \qquad (3.8)$$

where “x” is the weight loss of the raw material, “E_a” is the activation energy of the pyrolysis, “A” is the pre-exponentinal parameter, “R” is the universal gas constant “t” is the time of measurement, “m_i”, “m_t” and “m_f” are the initial weight of the raw material, the weight at “t” and final weight of sample, respectively.

3.4.1. The effect of the Me/Ni/ZSM-5 catalysts

The weight loss and dm/dt curves obtained with thermal and thermo-catalytic pyrolysis of raw material are shown in **Figure 3.15(a,b)**.



a)

b)

Figure 3.15(a,b)

Weight loss (a) and DTG curves (b) obtained with thermal and thermo-catalytic pyrolysis of raw material

Results well demonstrate that the tested Me/Ni/ZSM-5 catalysts had a significant effect to the decomposition of raw material. There were two peaks on the DTG curve; the first peak was occurred by the PET, while the second by the polyolefin decomposition.

The Ni/ZSM-5 catalyst can decrease the initial temperature of the decomposition in the highest degree, but the total decomposition needed more time and higher temperature in case of Ca/Ni/ZSM-5 catalyst compared to the case without catalyst **(Table 3.1)**. Presumably, it was caused by the slower decomposition processes in the last section of the weight loss curves (x < 25%) using Ca/Ni/ZSM-5 and Ce/Ni/ZSM-5 catalysts.

Table 3.1
Temperature values ($T_{5\%}$, T_{max} and $T_{95\%}$)

	$T_{5\%}$, °C	**T_{max1}, °C**	**T_{max2}, °C**	**$T_{95\%}$, °C**
No-catalyst	414	456	484	496
Ni/ZSM-5	345	435	475	493
Ca/Ni/ ZSM-5	368	449	476	673
Ce/Ni/ ZSM-5	282	440	479	649
La/Ni/ ZSM-5	358	445	476	526
Mg/Ni/ ZSM-5	327	445	477	536
Mn/Ni/ ZSM-5	386	446	481	509

Glancing the **Table 3.1**, it is clear, that the catalysts can reduce significantly the $T_{5\%}$ values. The lowest temperature was observed in case of Ce/Ni/ZSM-5 catalyst (282°C). The lowest peak maximum temperatures were found in case of the Ni/ZSM-5 catalyst (435 °C and 475 °C). Me/Ni/ZSM-5 catalysts can decrease the $T_{5\%}$ and T_{max} values, but due to less catalytic active sites of the Me/Ni/ZSM-5 catalyst, the decomposition finished at higher temperature. It is important to mentioned, that the lowest $T_{95\%}$ value was found in case of Mn/Ni/ZSM-5 catalyst among the bimetallic catalysts. **Figure 3.16** also shows the apparent activation energies. It was 208 kJ/mol without catalyst, which can be reduced by catalysts to the range of 134-162 kJ/mol.

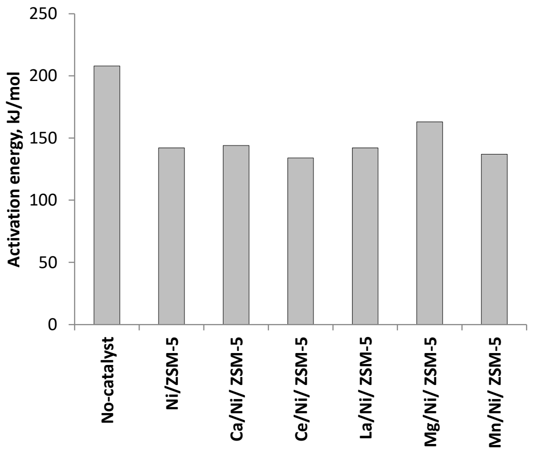
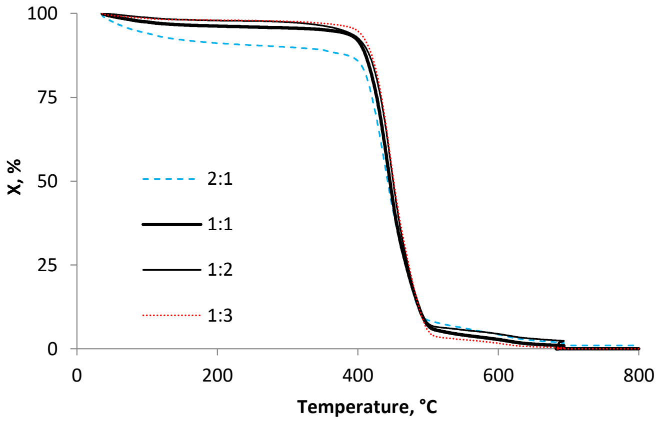


Figure 3.16
The calculated apparent activation energies

Not only low temperature values can be obtained by the use of Ce/Ni/ZSM-5 and La/Ni/ZSM-5 catalysts, but also these two catalysts can also significantly decrease the apparent activation energies.

3.4.2. The effect of catalyst to raw material ratio

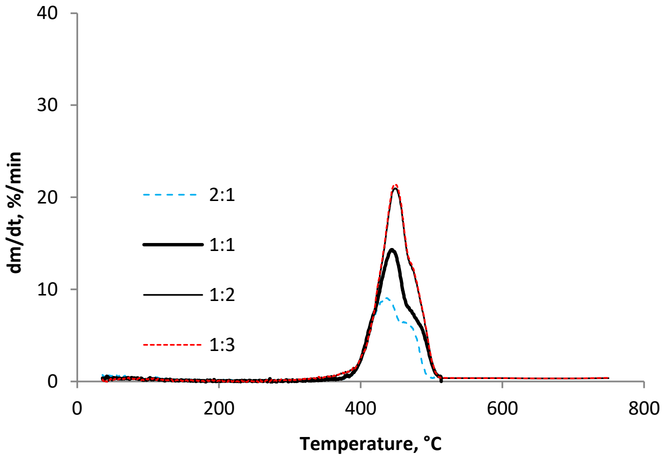
The catalyst to feedstock ratio is important to the pyrolysis reactions; therefore the effect of catalyst/raw material ratio was also investigated using La/Ni/ZSM-5 catalyst in ratio of 2:1, 1:1, 1:2 and 1:3. The weight loss and dm/dt are summarized in **Figure 3.17(a,b)**. It was concluded, that the ratio of the catalyst had a significant effect on the decomposition reactions, because the increasing in the amount of catalyst can decrease both the initial and T$_{max}$ temperatures of weight loss.



a)

Figure 3.17

Weight loss (a) and DTG curves (b) obtained with thermal and thermo-catalytic pyrolysis of raw material



b)

Figure 3.17(a,b)

Weight loss (a) and DTG curves (b) obtained with thermal and thermo-catalytic pyrolysis of raw material (cont.)

It is important to means that the value of $T_{95\%}$ can increased from 503 °C to 589 °C. It means that the temperature ranges become significantly wider as function of catalyst amount.

The $T_{5\%}$, T_{max} and $T_{95\%}$ values are summarized in **Table 3.2**. It is well shown, that the lowest initial temperature value was observed in case of 2:1 catalyst: raw material ratio (355°C), while the less $T_{95\%}$ was found in case of 1:3 ratio (503°C). The $T_{5\%}$ values increased, while the $T_{95\%}$ values decreased as function of the amount of raw material. It is important to mention, that due to the more catalytic active sites in case of higher catalyst/raw material ratio, the dm/dt values changed significantly as function of catalyst:raw material ratio, however the T_{max} values were very similar.

Table 3.2
Temperature values ($T_{5\%}$, T_{max} and $T_{95\%}$)

Catalyst/Raw material ratio	**$T_{5\%}$, °C**	**T_{max}, °C**	**$T_{95\%}$, °C**
2:1	355	441	589
1:1	359	444	525
1:2	376	448	579
1:3	400	450	503

Figure 3.18 shows the calculated activation energies using different catalyst: raw material ratios.

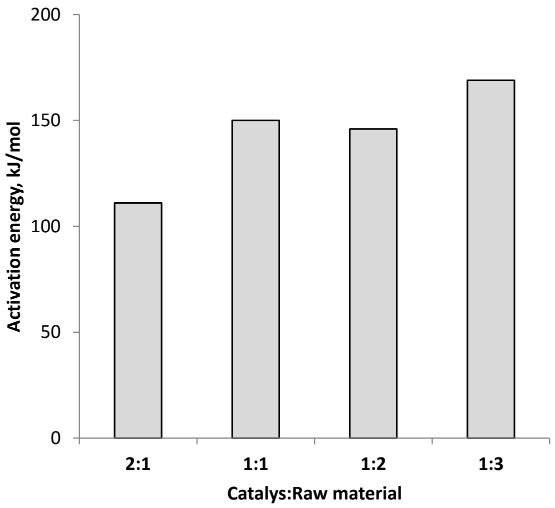


Figure 3.18
The calculated apparent activation energies

In one hand, the lowest activation energy was found at the highest catalyst to feedstock ratio, because of the above-mentioned reasons. On the other hand, the use of such high ratio of catalyst to feedstock is economically unfavourable due to the catalyst price; but more calculation is needed to optimize the catalyst: raw material ratio, because of the favourable effect of catalysts to the energy needed to the decomposition.

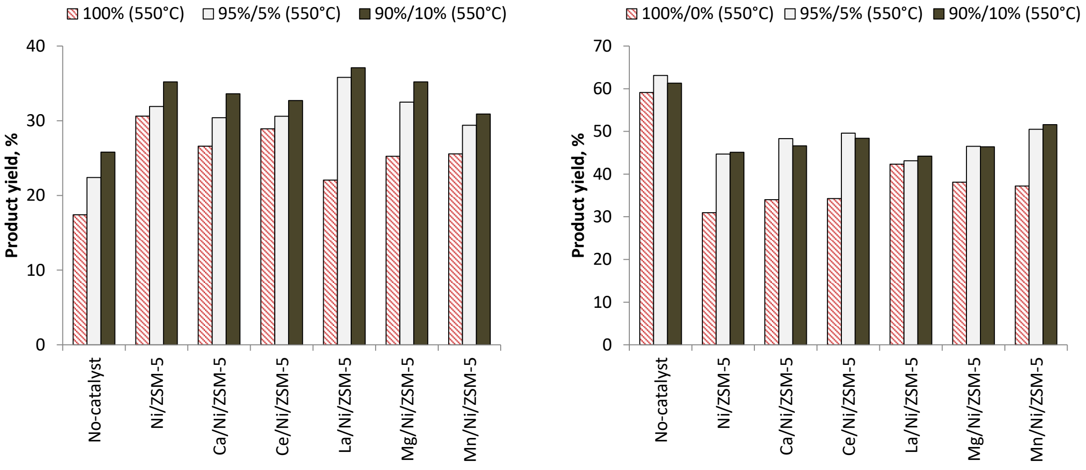
3.5. Pyrolysis of MPW in horizontal tubular reactor without steam

In this chapter the pyrolysis of municipal plastic waste is investigated in tubular reactor without steam using different Me/Ni/ZSM-5 catalysts to improve the syngas yield.

3.5.1. In nitrogen and partial oxidation on Ni/Me/ZSM-5 catalyst

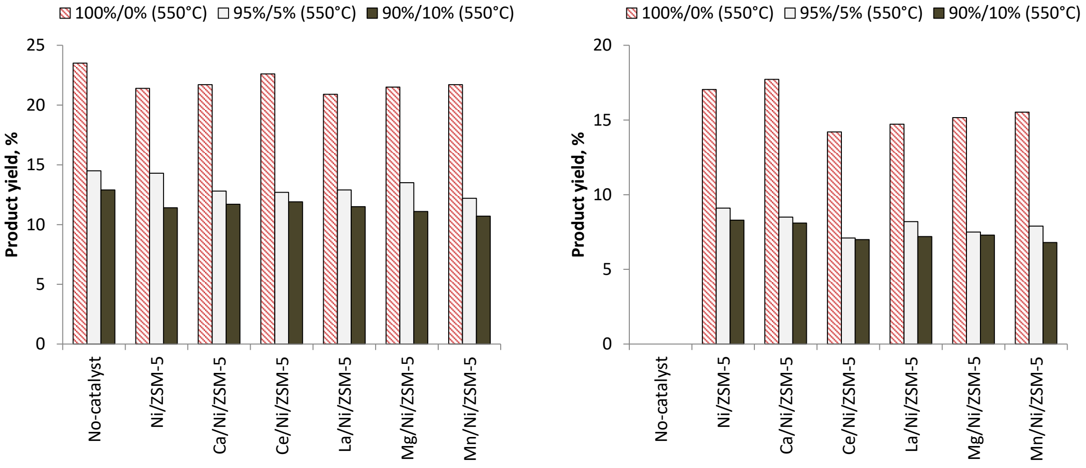
3.5.1.1. Product yields

The product yields using different nitrogen/oxygen ratio at 550 °C and 850 °C are shown in **Figures 3.19 and 3.20**. 100%/0%, 95%/5% and 90%/10% of N_2/O_2 atmosphere ratios were studied in the presence of different catalysts in order to investigate their influence on the product yields. Furthermore, the products from catalytic pyrolysis were compared with the process without catalyst. At temperature of 550 °C, the reported data showed that highest gas yield with N_2/O_2 ratio of 95%/5% and 90%/10% was obtained in the presence of La and Mg catalysts (35.8%, 32.5% and 37.1%, 35.2%) respecively. While, the gas yields were slightly decreased by the addition of Ce, Ca and Mn promoters. In contrast, the maximum gas yield for the pure N_2 atmosphere (100%/0% of N_2/O_2) was obtained over Ni/ZSM-5 catalyst. The addition of second metals led to slight decreasing for all promoters' type. Regarding to the influence of N_2/O_2 ratio, a little increase in the gas products were found with 90%/10% for all catalyst type and even for the non-catalytic process. Moreover, the results showed that presence of O_2 in the carrier gas could increase the gas yields compared to the pure N_2 (100%/0%). This can be attributed to the more partial oxidation reactions. However, the increasing in reaction temperature led to significant increasing of gases for all atmospheres. Definitely high pyrolysis temperature promoted the more cracking of raw materials and resulted in smaller compounds. At N_2/O_2 ratios of 100%/0%, 95%/5% and 90%/10%, the maximum gas yield was achieved over Ni/ZSM-5 catalyst at 850 °C.



Gases

Pyrolysis oil

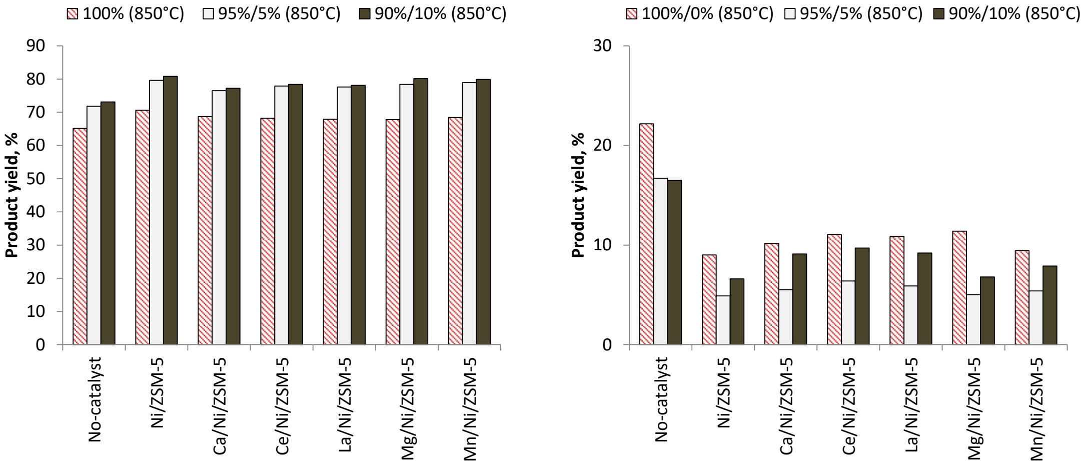


Char

Carbon deposition

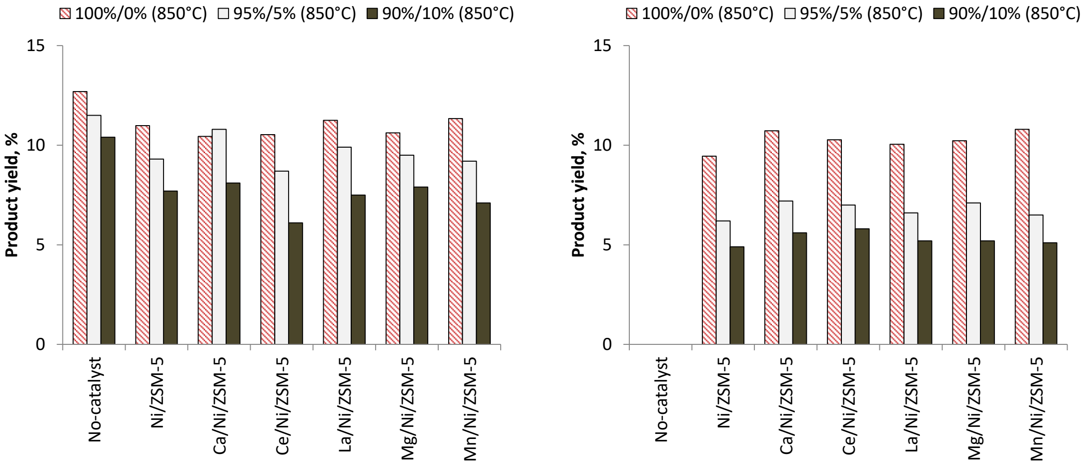
Figure 3.19
Product yields using different nitrogen/oxygen ratio at 550°C

Catalysts, temperature and O_2 atmosphere have also influenced the pyrolysis oil product. Generally, increasing of O_2 content with pyrolysis temperature led to lowering of oil yields over the different used catalysts. Moreover, running the process with catalysts caused notable decreasing of oil yields. High pyrolysis temperature and acidic property of the catalysts were behind that decreasing. However, the maximum pyrolysis oil product was obtained over the non-catalytic process with product yield of 63.1% at N_2/O_2 ratio of 95%/5% (at 550 °C). While, for catalytic pyrolysis, Mn supported ZSM-5 catalyst produced the highest oil (51.6%) at 10% content of O_2 atmosphere and low reaction temperature. The oil yields at 850 °C was in the range of 9.0-11.4% using 100%/0% N_2/O_2, 4.9-6.4 % in case of 95%/5% N_2/O_2 and 6.6-9.7 % over 90%/10% N_2/O_2 in the presence of catalysts.



Gases

Pyrolysis oil



Char

Carbon deposition

Figure 3.20

Product yields using different nitrogen/oxygen ratio at 850°C

Regarding to char yield, introducing the catalyst to the process resulted in slight decreasing of char product over the different N_2/O_2 ratios and decomposition temperatures. The maximum char yield was obtained without catalyst at 550 °C with N_2/O_2 ratio of 100%/0%. This can be contributed to the less cracking reactions in the absence of catalyst and low reaction temperature. One the other hand, the maximum amount of char yield for catalytic pyrolysis was reported in the presence of Ni/ZSM-5 catalyst at low temperature and 100%/0% of N_2/O_2 ratio.

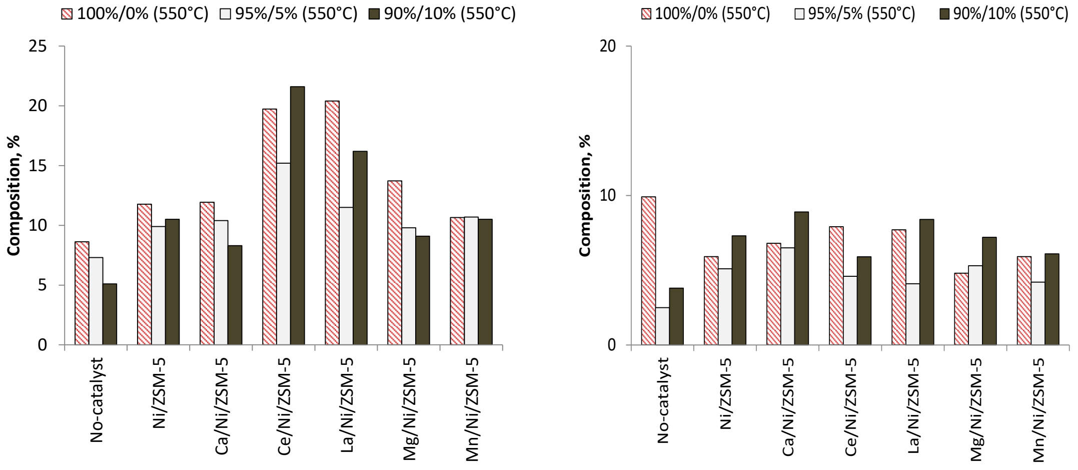
Furthermore, increasing of O_2 content in the process atmosphere led to decreasing of carbon deposition on the catalyst surface. Boudouard reaction was beyond that phenomena which was confirmed by the excess CO_2. Comparing the two reaction temperature and various N_2/O_2 ratios, the carbon deposition was reduced by rising the temperature and O_2 content. This is due to the reverse Boudouard reaction at elevated temperature. However, the carbon deposition over the different catalysts was in the range of 7.0 - 17.7 % (at 550 °C) and 4.9 -10.8 % (at 850 °C).

3.5.1.2. Gases

Figures 3.21 and 3.22 summarize the composition of gases using Me/Ni/ZSM-5 catalysts with different temperatures. H_2, CO, CO_2, CH_4 and hydrocarbons from C_2-C_5 are the main compositions of product gas. At low temperature of 550 °C, data showed that the oxygen content in the carrier gas can significantly influenced the concentration of H_2 and CO_2 in the gas yield. At N_2/O_2 ratio of 100%/0%, the maximum H_2 yield was reported over the second metals of Ce and La. The addition of 5% oxygen to the carrier gas resulted in decreasing of H_2 concentration for both catalytic and non catalytic processes. Increasing the oxygen content from 5 % to 10 % led to different trends as the hydrogen concentration was increased in case of Ni/ZSM-5, Ce/Ni/ZSM-5 and La/Ni/ZSM-5 but decreased for Ca/Ni/ZSM-5 catalyst. On the other hand, Mg/Ni/ZSM-5 and Mn/Ni/ZSM-5 catalysts did not influence significantly the H_2 yield with changing the O_2 ratio from 5% to 10%. Ce/Ni/ZSM-5 and La/Ni/ZSM-5 catalysts produced the highest amount of H_2 for all ratios of N_2/O_2 (100%/0%, 95%/5% and 90%/10%). The maximum H_2 yield at 550 °C was obtained at 10 % oxygen content in the presence of Ce/Ni/ZSM-5 catalyst which was 21.6 %. Regarding to CO_2 in the catalytic process, the concentration was increased with changing the N_2/O_2 ratio from 100%/0% to 95%/5% but then decreased with higher oxygen content of 10%. The highest concentration of CO_2 (38.6%) was obtained with catalyts free process at N_2/O_2 ratio of 90%/10%. The oxidation reaction was the reason for that phenomena *(3.9)*.

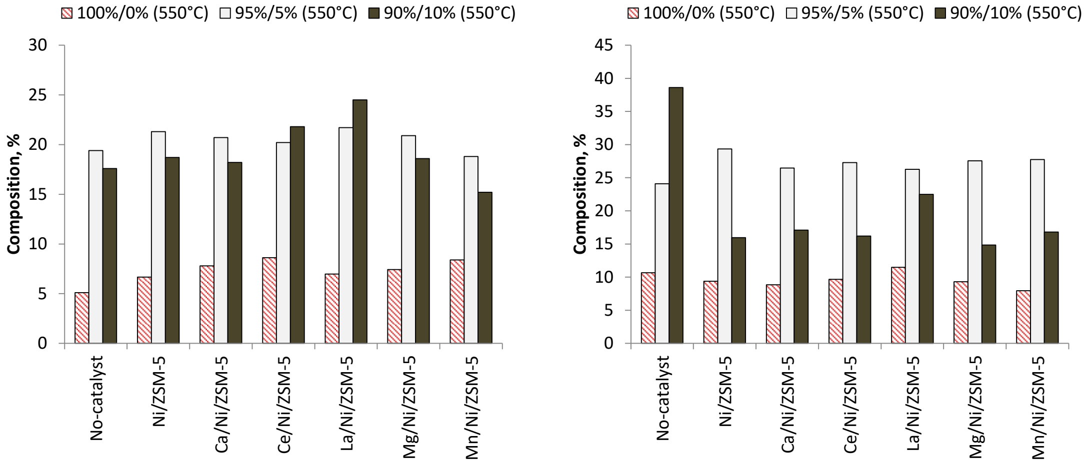
$$C_nH_m + n{+}m/2O_2 \rightarrow nCO_2 + m/2\ H_2O \qquad (3.9)$$

However, the CO_2 concentration was in the range of 8.0-29.3% in case of catalytic process, while, it was 10.7-38.6% for non-catalytic pyrolysis. On the other hand, visible effect was found in the concentration of CO by introducing the oxygen to the process compared to pure N_2 (100%/0%). In contrst, increasing the oxygen contnent from 5% to 10% did not influenced the CO yield at low temperature of 550 °C.



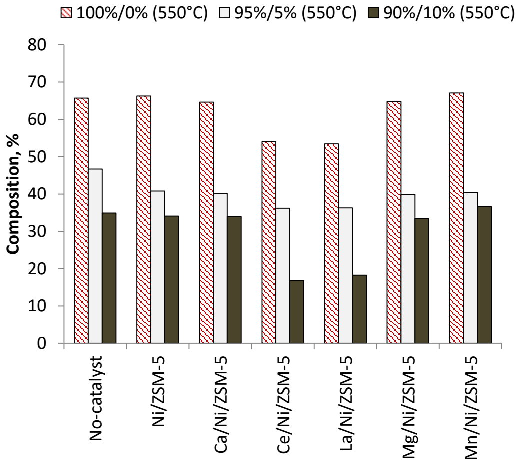
Hydrogen

Methane



CO

CO_2



C_2-C_5

Figure 3.21
The composition of gases using Me/Ni/ZSM-5 catalysts at 550°C using different nitrogen/oxygen ratio

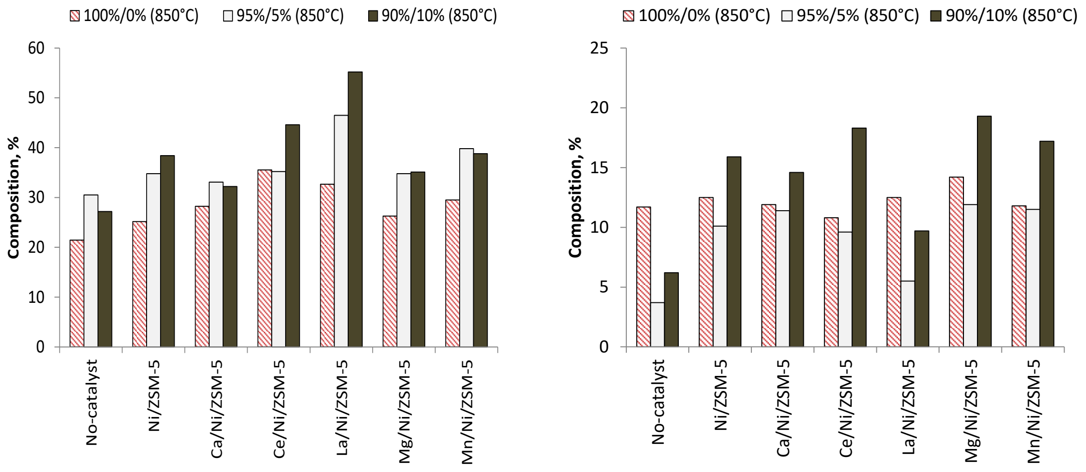
The methane concentration was slightly influenced by the N_2/O_2 ratio as it was decreased with increasing the O_2 content in the carrier gas. The maximum CH_4 yield (9.9%)

at 550°C was achieved in the absence of catalyst at N_2/O_2 ratio of 100%/0%. While, Ca/Ni/ZSM-5 catalyst produced the higest yield (8.9%) for catalytic processs at 10% of O_2 content. Regarding to C_2-C_6 (linear and brached) hydrocarbons in the gas product, the presence of HDPE, LDPE and PP in the raw materials was blamed for the formation of these hydrocarbons in the gas yield. Changing the ratio of N_2/O_2 also influnced thier concentration as it is decreased with oxygen. However, the maximum C_2-C_6 yield (67.1%) was found over Mn/Ni/ZSM-5 catalyst at low temperature and pure N_2 atmosphere. Rising the reaction temperature from 550 °C to 850 °C had a great influence on the gas composition especially hydrogen, methane and CO_2. Based on the obtained results, significant increasing in the hydrogen yield was found with increasing the temperature to 850°C over the different catalysts and even for the process without catalyst. The hydrogen concentration was in the range of 30.5-46.5 % in case of 95%/5% N_2/O_2 and in the range of 27.2-55.2 % in case of 90%/10% N_2/O_2. While, 100%/0% of N_2/O_2 ratio produced the lowest yield wich was 21.4-35.5 %. The highest yield of H_2 (55.2%) was reported over La/Ni/ZSM-5 catalyst with 10% of oxygen. The same trend was found with methane yield as the concentration was increased with reaction temperature. The CH_4 concentration was first decreased with the addition of oxygen compared to pure N_2 atmosphere (without O_2) but further increased with 10 % of O_2 content. However, Mg/Ni/ZSM-5 catalyst produced the maximum yield of methane at high temperature of 850 °C. This was attributed to the ability of catalyst for accelerating the methanization reactions. Moreover, the reverse reforming reactions are responsible for increasing of methane yield as shown in the equations.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{3.10}$$

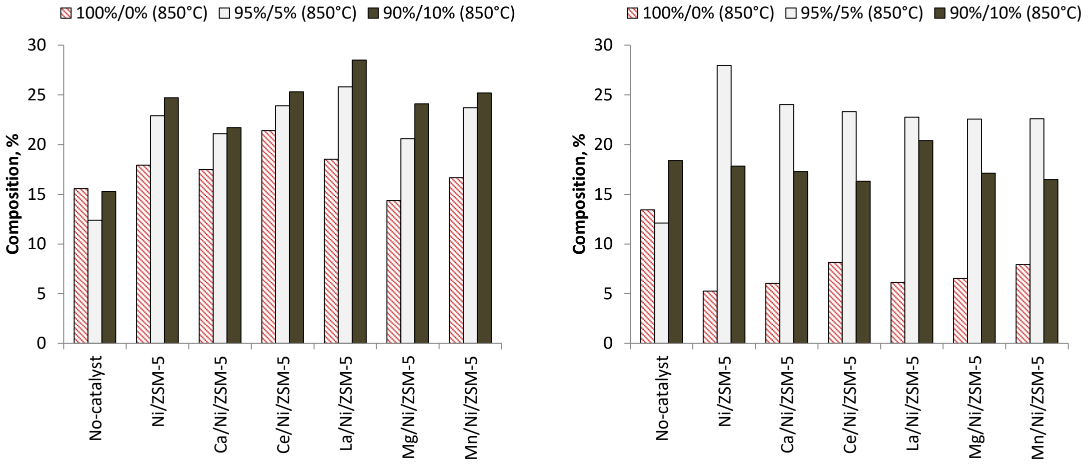
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{3.11}$$

Regarding to CO_2 yield, the result demonstrated that oxygen content of 5 % in the carrier gas resulted in the highest yield of CO_2 concentration for catalytic process in comparison to other N_2/O_2 ratios. While increasing of O_2 content can significantly influenced the CO_2 yield at 850 °C. The maximum CO_2 yield (28.0 %) at high temperature was obtained in the presence of Ni/ZSM-5 catalyst at N_2/O_2 ratio of 95%/5%.



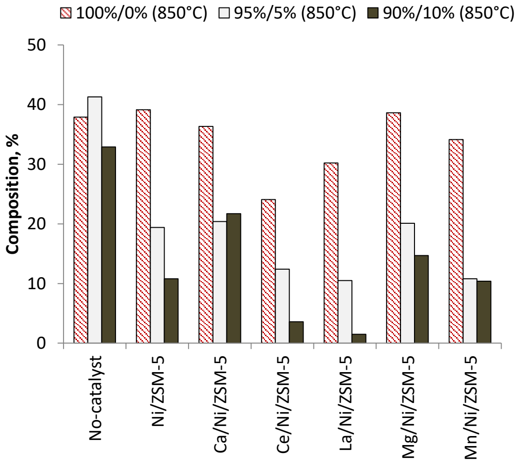
Hydrogen

Methane



CO

CO_2

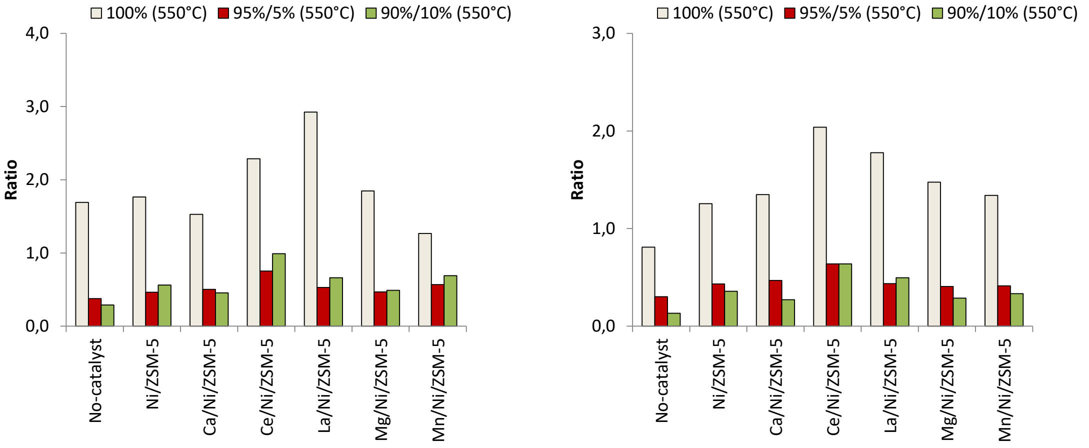


C_2-C_5

Figure 3.22
The composition of gases using Me/Ni/ZSM-5 catalysts at 850°C using different nitrogen/oxygen ratio

This increasing explains the high concentration of methane at high temperature espacialy in the presence of catalysts at any N_2/O_2 ratios. On the other hand, the concentration of CO at elevated temperature with catalysts was higher compared to CO_2 due to the Boudouard reactions. That is why the char depositon was decresing at 850 °C. Regarding to other hydrocarbons (C_2-C_5) in the gas yields, rising the temperature resulted in decreasing of their concentration for all N_2/O_2 ratios. Furthermore, the high oxygene content in the carrier gas could decreased the concentration of C_2-C_5 at 850 °C. Regardless of the O_2 content, the intermediates from the isomerization of these compounds are cracked at high temperature to form hydrogen and methane. The highest yield of C_2-C_5 hydrocarbons (41.3 %) at high temperature was reported with N_2/O_2 ratio of 95%/5% in the absence of catalysts.

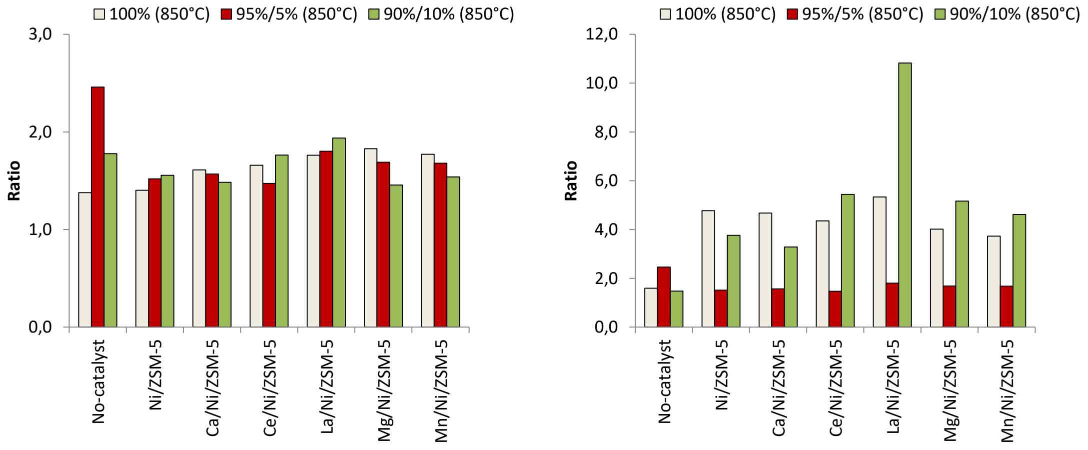
The ratio of H_2/CO and H_2/CO_2 in gases using Me/Ni/ZSM-5 catalysts with different nitrogen/oxygen ratio at 550°C and 850°C are shown in **Figures 3.23 and 3.24**. Based on the obtained data, the ratio of H_2/CO at 550 °C was the highest with pure N_2 carrier gas (100%) compared to other atmospheres. The addition of O_2 resulted in obvious decreasing of H_2/CO ratio especially with 95%/5% ratio of N_2/O_2. The highest H_2/CO ratio was found over La/Ni/ZSM-5 catalyst with 100 % of N_2 atmosphere. The same tendency was reported for the ratio of H_2/CO_2 as it is decreased with increasing the oxygen content and the maximum H_2/CO_2 ratio was also reported with 100%/0% of N_2/O_2 atmosphere. Ce/Ni/ZSM-5 catalyst product the highest H_2/CO_2 ratio among the various used catalysts.



Ratio of H_2/CO Ratio of H_2/CO_2

Figure 3.23
The ratio of H_2/CO and H_2/CO_2 in gases using Me/Ni/ZSM-5 catalysts with different temperatures and atmospheres at 550°C

When the reactor temperature rised to 850 °C, the results showed that maximum ratio of H_2/CO was obtained with the non-catalytic process at 95%/5% of N_2/O_2 ratio. While, no significant change in the H_2/CO ratio for the catalytic process with changing the oxygen content in the atmosphere. La/Ni/ZSM-5 catalyst had the highest ratio of H_2/CO in the catalytic process which was achieved at O_2 content of 10 %. On the other hand, the maximum ratio of H_2/CO_2 at 850 °C was reported for the catalytic process in the presence of La metal at N_2/O_2 ratio of 90%/10%. In contrast, the lowest H_2/CO_2 ratio at high temperature was observed without catalyst.



Ratio of H_2/CO Ratio of H_2/CO_2

Figure 3.24
The ratio of H_2/CO and H_2/CO_2 in gases using Me/Ni/ZSM-5 catalysts with different temperatures using different nitrogen/oxygen ratio at 850°C

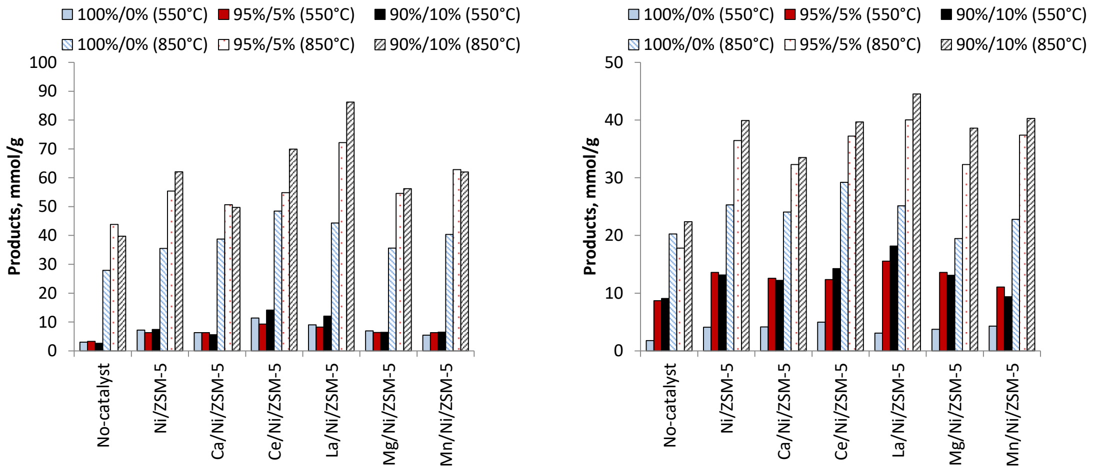
Figure 3.25 summarizes the yields of hydrogen and carbon-monoxide using Me/Ni/ZSM-5 catalysts at different temperatures (550°C and 850°C) with different nitrogen/oxygen ratios. It can be seen that temperatures with bimetallic catalysts have a great influence on the syngas yields for all ratios of N_2/O_2. Higher reaction temperature promoted the more reaction rate of partial oxidation due to the presence of O_2 in the atmosphere which led to more yield of syngas (H_2 and CO) as shown in the equations *(3.12-3.14)*.

$$C_nH_m + n/2\ O_2 \rightarrow n\ CO\ \ m/2\ H_2 \tag{3.12}$$

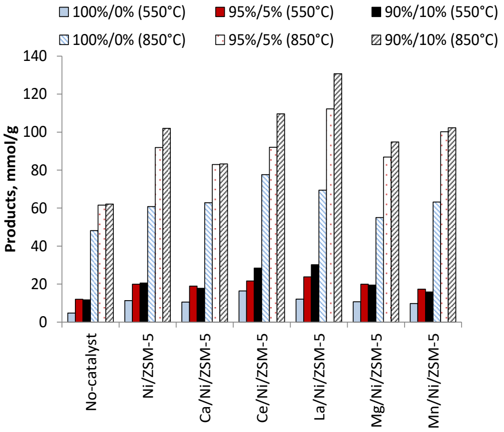
$$C_nH_m + n/2\ H_2O \rightarrow n\ CO + (m+n)/2\ H_2 \tag{3.13}$$

$$C_nH_m + n\ CO_2 \rightarrow n\ CO + m/2\ H_2 \tag{3.14}$$

The syngas yield was also higher in the absence of catalysts at 850 °C compared to 550 °C. Hydrogen and CO yield was enhanced in the presence of catalyst due to the higher cracking activity as a consequence of ZSM-5 supporter and second metal. Furthermore, Ni catalyst has the ability to increase the hydrogenation dehydrogenation reactions. Regarding to the effect of N_2/O_2 ratio, higher O_2 content led to more oxidation reactions which resulted in more CO_2 yield. The more CO_2 shifted the Boudouard reaction toward the formation of CO (Le Chatalier's principle).



Hydrogen CO



Syngas

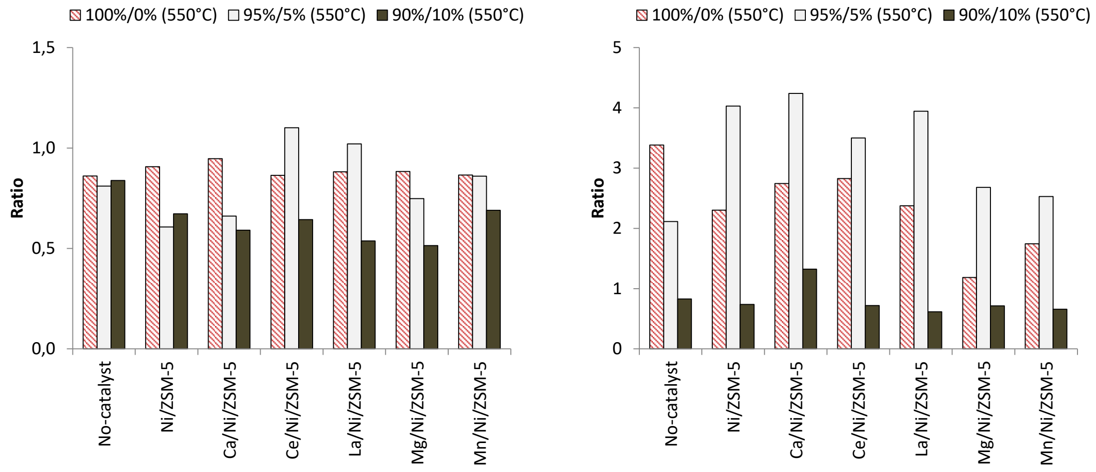
Figure 3.25
The yields of hydrogen and carbon-monoxide using Me/Ni/ZSM-5 catalysts with different temperatures using different nitrogen/oxygen ratio

Hence, more CO was found in the gas product at higher oxygen content in the atmosphere. Comparing the effect of second promoters, Ce and La produced the highest yield of hydrogen and CO. However, the maximum syngas product (130.7 mmol/g) was obtained in the presence of La/Ni/ZSM-5 catalyst at 850 °C and 90%/10% of N_2/O_2 ratio.

While, the lowest yield (9.7 mmol/g) of syngas was found over Mn/Ni/ZSM-5 catalyst at 550°C with pure N_2 atmosphere (100%/0% N_2/O_2). The effect of oxygen carrier gas on syngas production has also been reported by Zhifeng Hu etl al. [104] for the gasification of microalgae at temperature range of 600-900 °C. They also observed that increasing of oxygen content in the carrier gas led to increasing of CO yield but further increasing of oxygen carrier resulted in deacreasing of syngas and CH_4 yields.

3.5.1.3. Pyrolysis oil

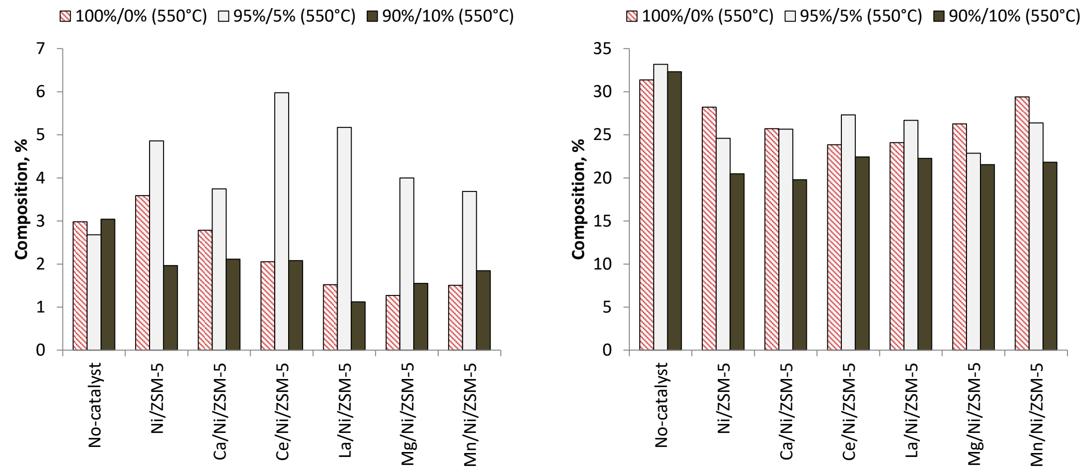
The composition of pyrolysis oil using Me/Ni/ZSM-5 catalysts with different nitrogen/oxygen ratios at 550 °C and 850°C are shown in **Figures 3.26 and 3.27**. N-paraffin, n-olefins, aromatics, oxygenated and branched compounds represent the main compositions of oil yield. Regading to other compositions, oil contained phenolic and oxygenated compounds. The more oxygen content (10 %) in the carrier gas had negative effect on the concentration of phenol for both temperatures. At low temperature, the maximum amount of phenol was found in the presence of Ce and La catalysts at 95%/5% of N_2/O_2 which was in the range of (5.2-6.0). In contrast, the maximum phenol contentration (6.1) at 850 °C was obtained without catalyst with 5% O_2 content.



n-paraffin/n-olefin

single ring/multiring

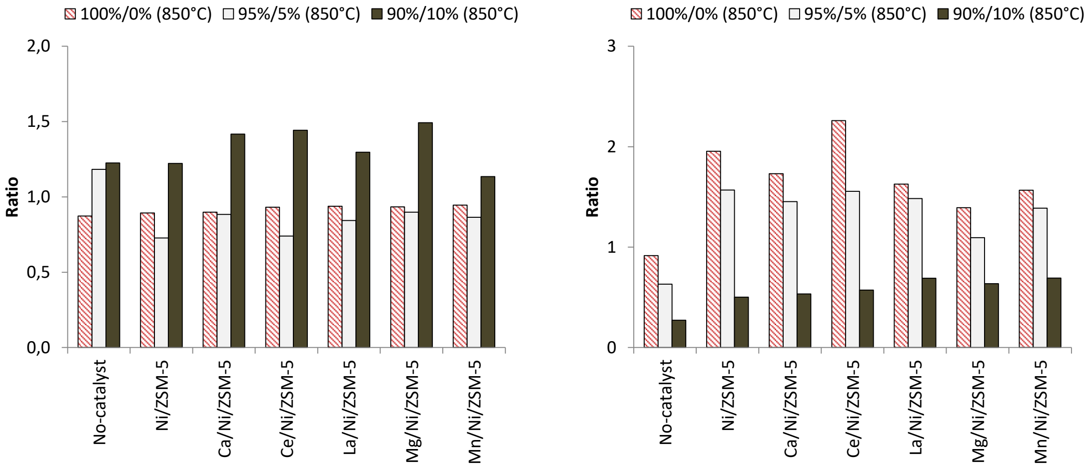
Figure 3.26
The composition of pyrolysis oil using Me/Ni/ZSM-5 catalysts with different nitrogen/oxygen ratios at 550°C



Phenol Aldehide, keton, carboxilic acid

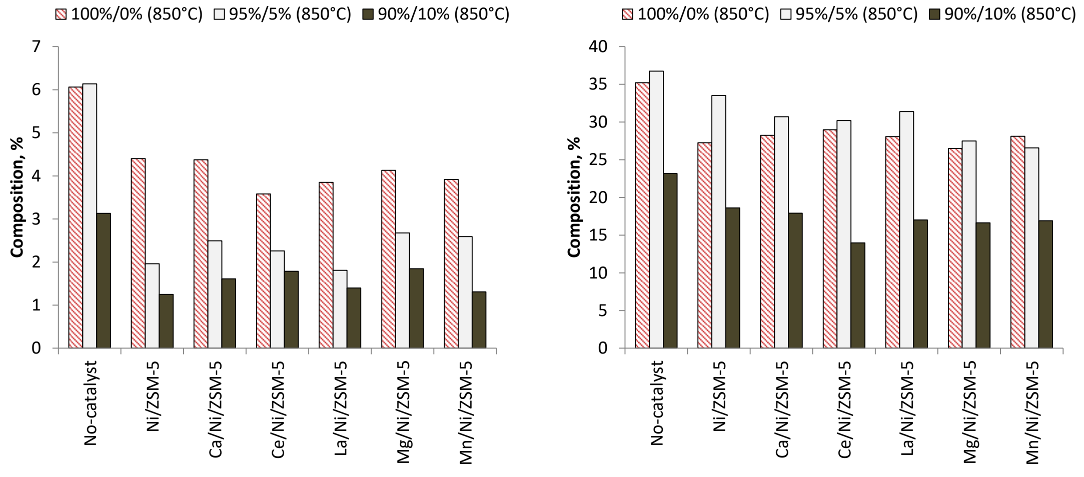
Figure 3.26
The composition of pyrolysis oil using Me/Ni/ZSM-5 catalysts with different nitrogen/oxygen ratios at 550°C (cont.)

It is important to remark that introducing the Me/catalyst to the process at 850 °C resulted in decreasing of phenol concentration at all N_2/O_2 ratios of 100%/0%, 95%/5% and 90%/10%. The same trend was found at 550 °C and 10 % of oxygen content. On the other hand, running the process without catalyst is favourable for the formation of benzoic acid and terephthalic acid at both temperatures.



n-paraffin/n-olefin single ring/multiring

Figure 3.27
The composition of pyrolysis oil using Me/Ni/ZSM-5 catalysts with different nitrogen/oxygen ratios at 850°C



Phenol

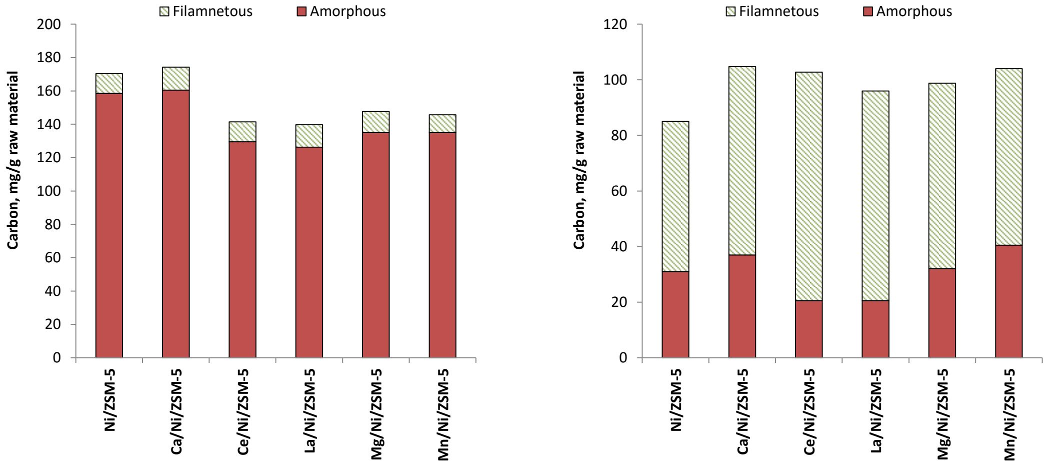
Aldehide, keton, carboxilic acid

Figure 3.27
The composition of pyrolysis oil using Me/Ni/ZSM-5 catalysts with different nitrogen/oxygen ratios at 850°C (cont.)

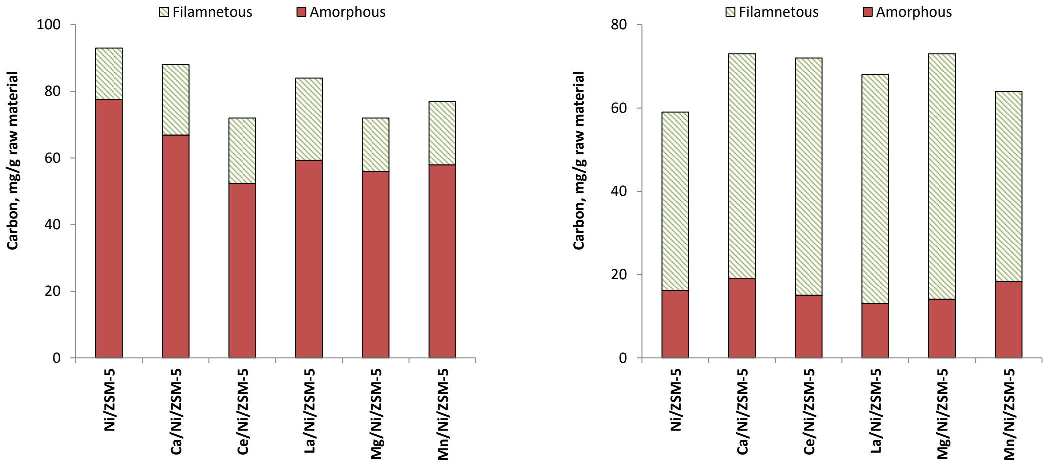
The presence of catalyst at 850 °C resulted in decreasing of oxygenated compounds at all N_2/O_2 ratios. Furthermore, the more O_2 content resulted in lowering the concentration of the oxygenated compounds. However, the maximum yield of oxygenated compounds (aldehide, keton, carboxilic acid) was obtained in the absence of catalyst at 550 °C and N_2/O_2 ratio of 95%/5%. It was observed that hydrogenation reaction was taken place in the presence of catalyst at 850 °C and 10% of O_2 content which led to increasing of H_2 concentration and reducing the concentration of oxygenated compounds.

3.5.1.4. Production of carbon nanotubes

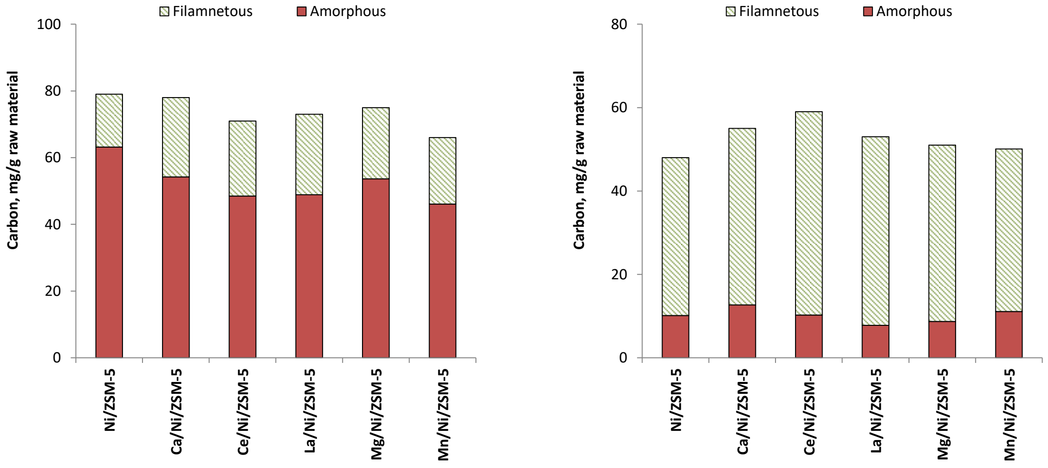
Figure 3.28 illustrates the TPO results for the used catalysts. Based on the obtained data, two types of carbon deposition were found on the catalyst surface, which are filamentos and amourphous. It is seen that low temperature of 550 °C and zero oxygen content are favoured for the formation of amorphous carbon on the catalyst surface.



550°C, 100%/0% N_2/O_2 850°C, 100%/0% N_2/O_2



550°C, 95%/5% N_2/O_2 850°C, 95%/5% N_2/O_2

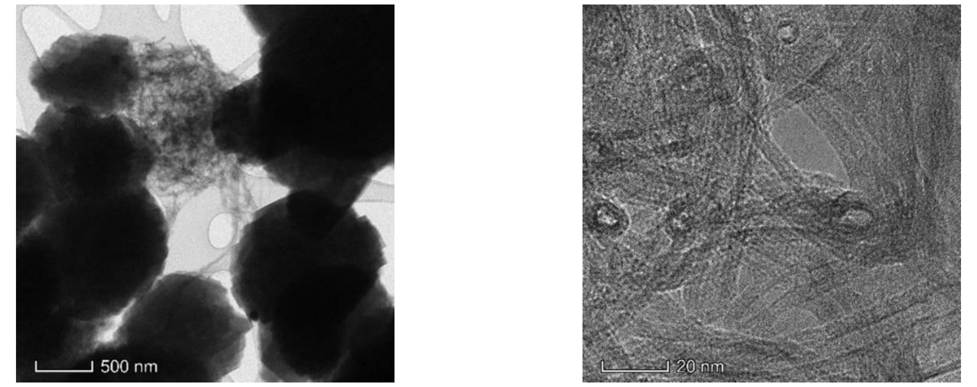


550°C, 90%/10% N_2/O_2 850°C, 90%/10% N_2/O_2

Figure 3.28
TPO result of catalyst after pyrolysis

Rising the reaction temperature to 850 °C resulted in clear decreasing of amorphous carbon. While, opposite tendency was reported for the filamentous carbon as it is increased with temperature. In general, the amount of carbonaceous materials are relatively lower at 850 °C compared to 550 °C. The carbon reduction at high temperature was beyond that phenomeina. The addition of oxygen to the process atmosphere resulted in more reduction of amorphous carbon, especially at high reaction temperature. In contrast, oxygen in the carrier gas led to increasing of filamentous ratio over the different used catalysts. Further decreasing of the carbonaceous materilas was found with rising the O_2 content to 10 % at both temperatures which may attibuted to the more oxidation reatios. However, the same trend was observed for the ratio of filamentous carbon at high reaction temperature of 850 °C. The highest ratio of amorphous carbon at 95%N_2/5%O_2 and 90%N_2/10%O_2 ratios was achieved over Ni/ZSM-5 catalyst at 550 °C. while, the lowest ratio of amorphous carbon was reported with La/Ni/ZSM-5 catalyst at oxygen content of 10 % and 850 °C.

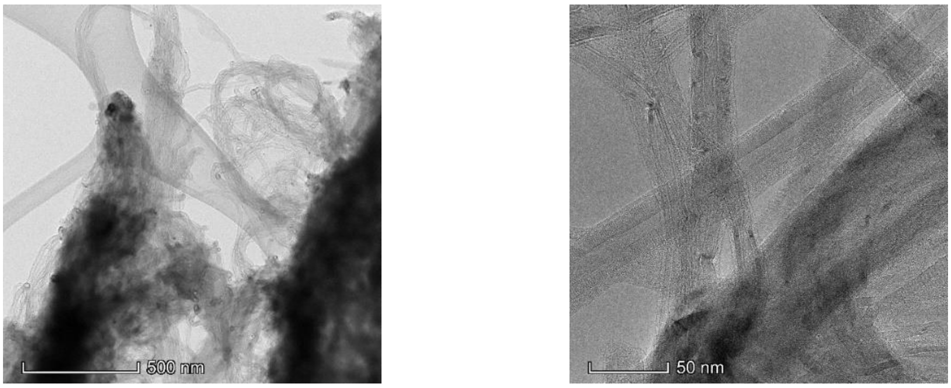
Figure 3.29 shows the TEM images of CNTs on selected catalysts after the pyrolysis experiments. The TEM results showed the formation of CNTs on the catalyst surface of Ce/Ni/ZSM-5. When 100 %/0 % of N_2/O_2 atmosphere was used, darker spots were visible on the image. Increasing the oxygen content to 5 % at high temperature of 850 °C resulted in decreasing of darker spots. However, further increasing of oxygen content to 10 % led to darker spots compared to 95 %/5 % of N_2/O_2 ratio.



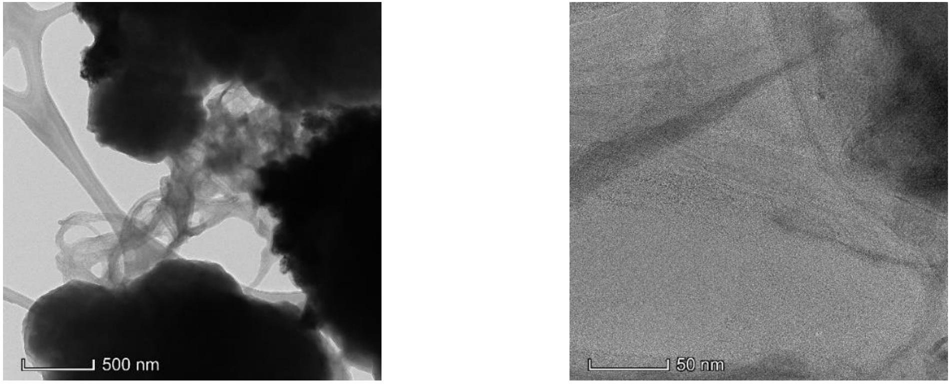
Ce/Ni/ZSM-5, 850°C, 100%/0% N_2/O_2

Ce/Ni/ZSM-5, 850°C, 100%/0% N_2/O_2

Figure 3.29
TEM images of CNTs on the catalyst surface



Ce/Ni/ZSM-5, 850°C, 95%/5% N_2/O_2 Ce/Ni/ZSM-5, 850°C, 95%/5% N_2/O_2



Ce/Ni/ZSM-5, 850°C, 90%/10% N_2/O_2 Ce/Ni/ZSM-5, 850°C, 100%/10% N_2/O_2

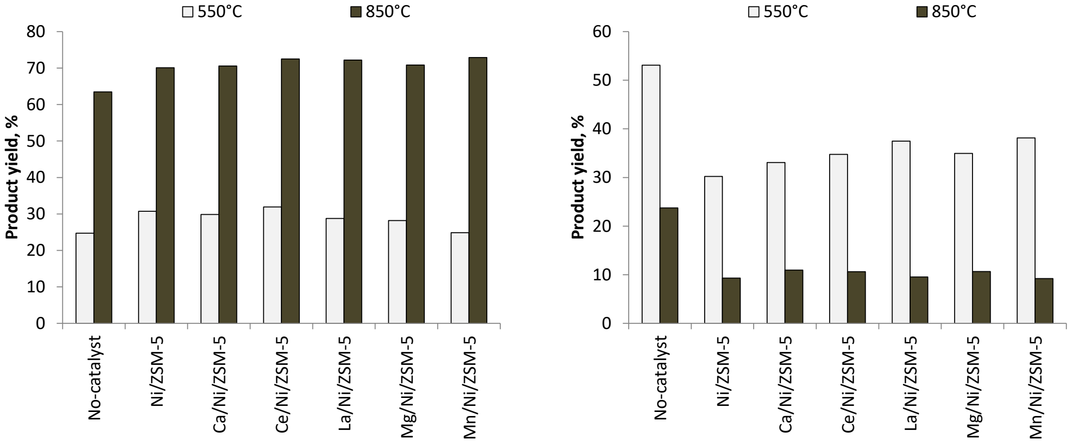
Figure 3.29
TEM images of CNTs on the catalyst surface (cont.)

3.5.2. In nitrogen in the presence of dolomite on Ni/Me/ZSM-5 catalyst

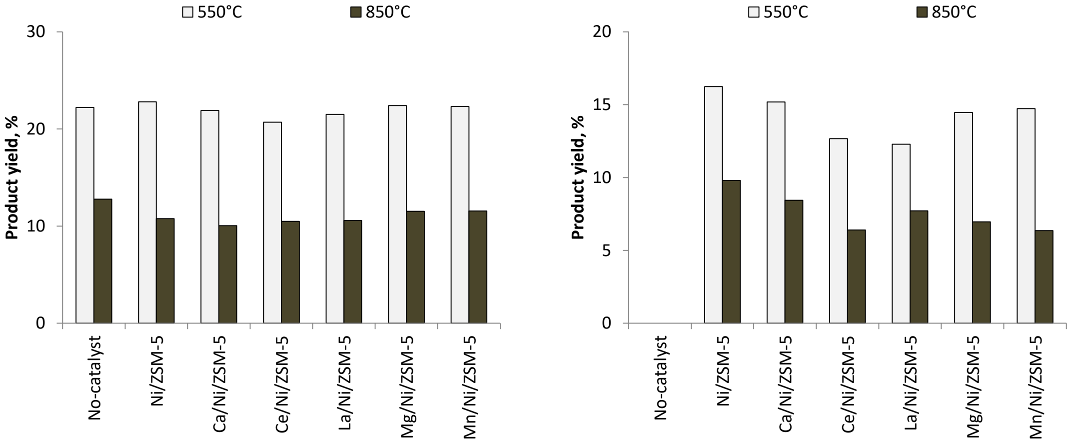
In this chapter two different reaction temperatures of 550 °C and 850 °C with various catalyst type were used to predict their influence on the pyrolysis yields and product compositions. For catalytic pyrolysis Ni-ZSM-5 and Me/Ni-ZSM-5 (Me=Ce, Ca, La, Mg and Mn) have been investigated. Furthermore, dolomite was used to generate CO_2 for in-situ dry reforming process. In addition, the product from catalytic process was compared with the product from thermal process.

3.5.2.1. Product yields

Figure 3.30 illustrates the product yields (gases, oil, and char) and carbon deposition on the catalyst surface at 550 °C and 850 °C. The results showed that introducing the cata-lyst to the reactor led to visible increasing of gases over the different used catalysts. That phenomena was due to the property of ZSM-5 catalyst for cracking the long polymer chain of raw material and converting them to smaller species (gases). However, the highest gas yield at low pyrolysis temperature of 550 °C was obtained in the presence of second promoter of Ce over Ni/ZSM-5 catalyst which was 31.9 %. On the other hand, liquid product was dropped by the addition of catalysts and the maximum yield (53.1 %) was found in the absence of catalyst.



Gases Pyrolysis oil



Char Carbon deposition

Figure 3.30
Product yields using different temperatures

The amount of char was almost same for all catalyst type at 550 °C; it was in the range of 20.7-22.8 %. Temperature has also clear influence on the carbon deposition on the catalyst surface as the higher temperature resulted in decreasing of carbon materials over the various catalysts. The presence of dolomite generates more CO_2 which reacts with carbonaceous materials at high temperature and reduced the amount of deposited carbon ($C + CO_2= 2CO$). However, the maximum carbon deposition was reported over Ni/ZSM-5 catalyst which was 16.2 %. When the reactor temperature elevated to 850 °C, the gases yield was significantly increased. While, opposite trend was observed for the pyrolysis oil at higher temperature. The more decomposition and cracking reaction of raw materials at high temperature were behind the high gases in the product yields. Moreover, the dolomite at high temperature promoted the more dry reforming reactions due to the more CO_2 production.

The maximum gas yield was reported over Ce/Ni/ZSM-5 and Mn/Ni/ZSM-5 catalysts which were 72.5 and 72.9 % respectively. It can conclude that second metal incorporation could enhance the catalyst performance towards gas production. In contrast, the char yield was reduced with temperature for both catalytic and non-catalytic processes due to the gasification reactions at 850 °C. The highest amount of char product at 850 °C was obtained in the absence of catalyst which was 12.8 %, while second promoters of Mg and Mn produced the maximu char in case of catalytic pyrolysis.

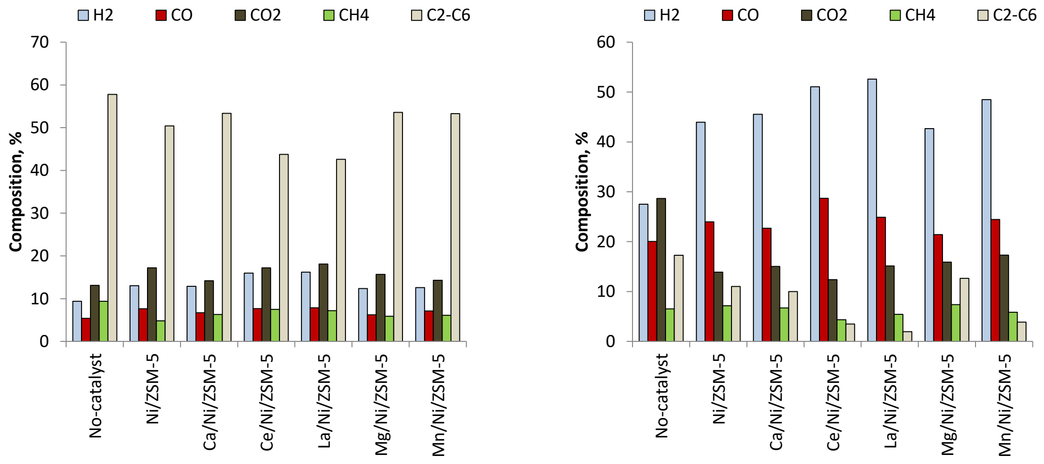
3.5.2.2. Gases

Figure 3.31 shows the main gas compositions in the product yield which contain hydrogen, carbon monoxide, carbon dioxide, methane and hydrocarbons from C_2 to C_6. Despite of the catalyst effect, the GC data showed that temperature had positive influence on the concenteration of hydrogen and carbon monoxide due to the notable increasing with temperature. At low temperature of 550 °C, the maximum yield of H_2 and CO was reported in the presence of Ce and La promoters which were 16.0 %, 7.7 % and 16.2 %, 7.9 % respectively. Regarding to CO_2 yield, Ni/ZSM-5, Ce/Ni/ZSM-5 and La/Ni/ZSM-5 catalysts produced the maximum concentration at 550 °C. The concentration of hydrogen and carbon monoxide were increased with increasing the reactor temperature to 850 °C. At high temperature, hydrocarbons can produce more hydrogen based on the *(3.1)* reaction. Furthermore, the calcinations reactions of dolomite at high temperature generate more CO_2 and this led to more dry reforming reactions *(3.15)*.

$$C_xH_y+xCO_2 \rightarrow 2xCO+y/2H_2 \tag{3.15}$$

This was more confirmed by the decreasing of hydrocarbons (C_2-C_6) at 850 °C over the various used catalysts and even for non-catalytic process. Also, the maximum yield was obtained over Ce and La catalysts which were 51.1 % and 52.6 for H_2 and 28.7 % and 24.9 % in case of CO. Comparing the performance of the various used catalysts in terms of H_2 yield, Mg/Ni/ZSM-5 catalyst showed the lowest influence due to the lower H_2 product which were 12.4 % and 42.7 % at 550 °C and 850 °C respectively.

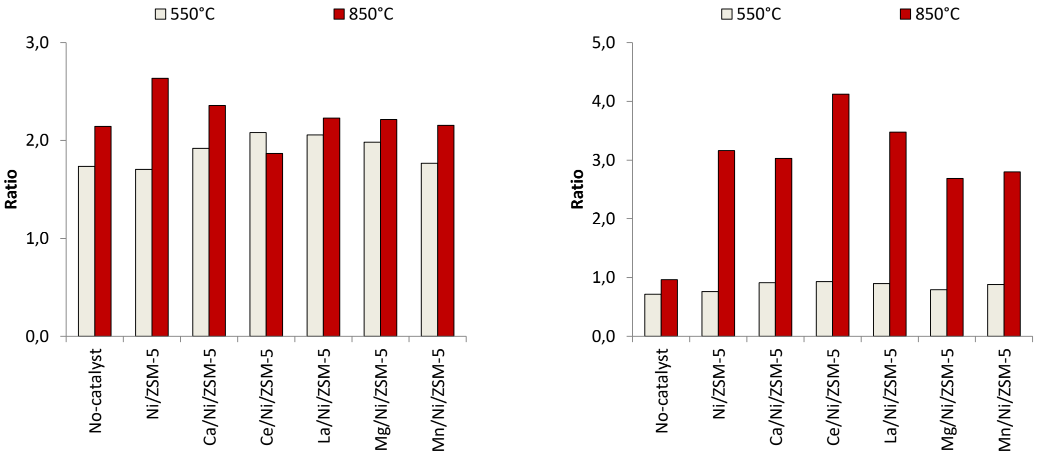
Regarding to CH_4 concentration in the gas composition, no significant difference in the CH_4 yield was found among the second metal promters as it was in the range of 5.9-7.5 %. Comparing the two temperatures, low temperature of 550 °C produced the maximum CH_4 concentration with 9.4 % yield in the absence of catalyst. However, different trends were observed over the CH_4 concentration in the presence of dolomite plus catalysts at 850 °C. The CH_4 product was increased in case of Ni/ZSM-5 and Mg/Ni/ZSM-5 catalysts, while it is decreased with other catalysts. The methane yield in the gas compositins was a consequence of methanization reaction ($C+2H_2 \rightarrow CH_4$).



550°C

850°C

Figure 3.31
The composition of gases using Me/Ni/ZSM-5 catalysts with different temperatures

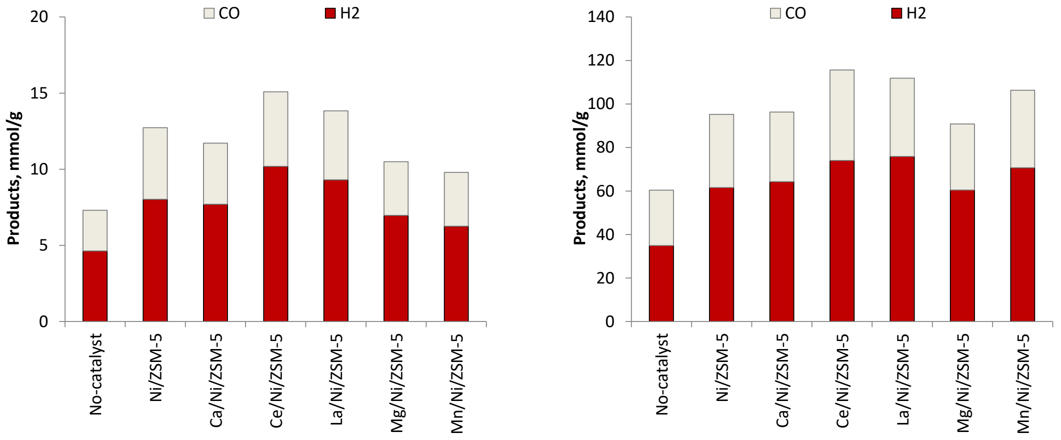


Ratio of H_2/CO

Ratio of H_2/CO_2

Figure 3.32
The ratio of H_2/CO and H_2/CO_2 in gases using Me/Ni/ZSM-5 catalysts with different temperatures

The ratio of H_2/CO and H_2/CO_2 are shown in **Figure 3.32**. Results demonsterted that temperature had positive effect on both ratios of H_2/CO and H_2/CO_2. At low temperture, introducing the second promters to process resulted in more ratio of H_2/CO in comparison to catalyst without promoters. Generally, rising the temperature with dolomite presence resulted in more H_2/CO ratio. The maximum ratio of H_2/CO (2.6) was achieved over Ni/ZSM-5 catalyst at 850 °C. The same trend was reported for the H_2/CO_2 ratio as it increased with temperature. This phenomenon corresponds to the dry reforming of hydrocarbons at eleveated temperature due to the presence of dolomite in the reactor.



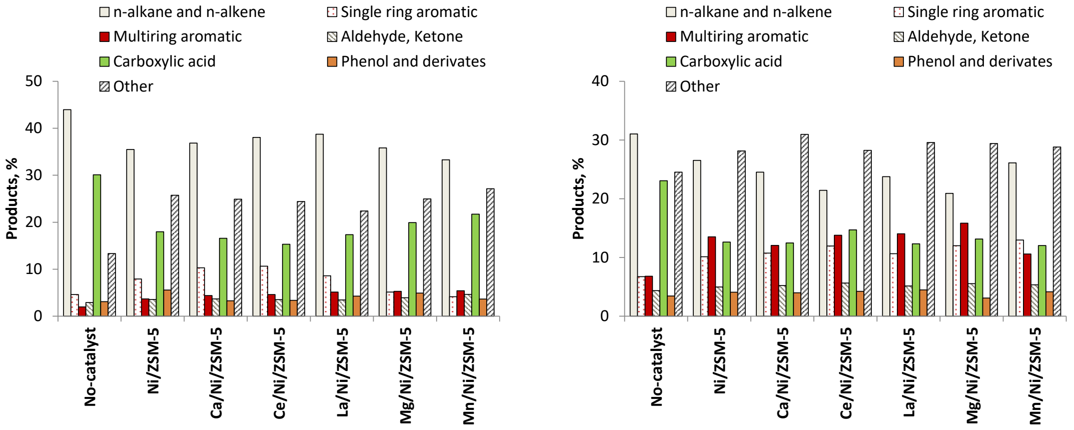
550°C 850°C

Figure 3.33
The yields of hydrogen and carbon-monoxide using Me/Ni/ZSM-5 catalysts with different temperatures

Temperature and catalyst type have also visible influnce on the syngas yields as shown in **Figure 3.33**. Regardless of the temperature effect, introducing the catalysts to the process led to clear increasing of syngas products at both temperatures (550 and 850 °C) comparing to the process without catalyst. Catalysts with dolomite can promted the gasification reaction which resulted in more syngas yield in the product. A similar trend has been reported by Rapagn et al. [105] for the hydrogen production from biomass, who observed that H_2 yield was increased from 43.6 vol% to 55.5 vol% by introducing the dolomite to the reactor. As it mentioned above, the CO_2 from dolomite decomposition could enhance the formation of hydrogen and carbon-monoxide especially at high temperature. However, the maximum syngas yield at 550 °C and 850 °C was found over Ce/Ni/ZSM-5 catalyst which was 15.1 and 115.6 mmol/g respectively. In contrast, the lowest effect for both hydrogen and carbon monoxide increasing in the presence of promters was reported with Mn/Ni/ZSM-5 at 550 °C and Mg/Ni/ZSM-5 catalyst at 850 °C.

3.5.2.3. Pyrolysis oil

The compositions of pyrolysis oil are representing in **Figure 3.34(a,b)**. Oil contained n-alkane, n-alkene, single and multi ring aromatic, oxygenated and branched compunds. Highly concentration of n-paraffin and n-olefin were found in the oil yields as a consequence of polyethylene presence in the feedstock. These compounds were higher in the absence of catalysts at both reaction temperatures. In case of catalytic process, the highest concetration of n-paraffin and n-olefin was observed over second metals of Ce and La promters at 550 °C which was 38.1 % and 38.7 %. The concentration of these compounds were decreased when the reactor temperature rised to 850 °C. On the other hand, the concentration of single and multi ring aromatic was increased with introducing the catalysts and a bit increased with increasing the remperature to 850 °C. This was attributed to the ZSM-5 presnce in the catalyst which promoted the aromatization reaction. However, the maximum contentration of single ring aromatic (13.0 %) was obtained with Mn/Ni/ZSM-5 catalyst at 850 °C, while the maximum yield of multi ring aromatic (15.8 %) was reported over Mg/Ni/ZSM-5 catalyst.



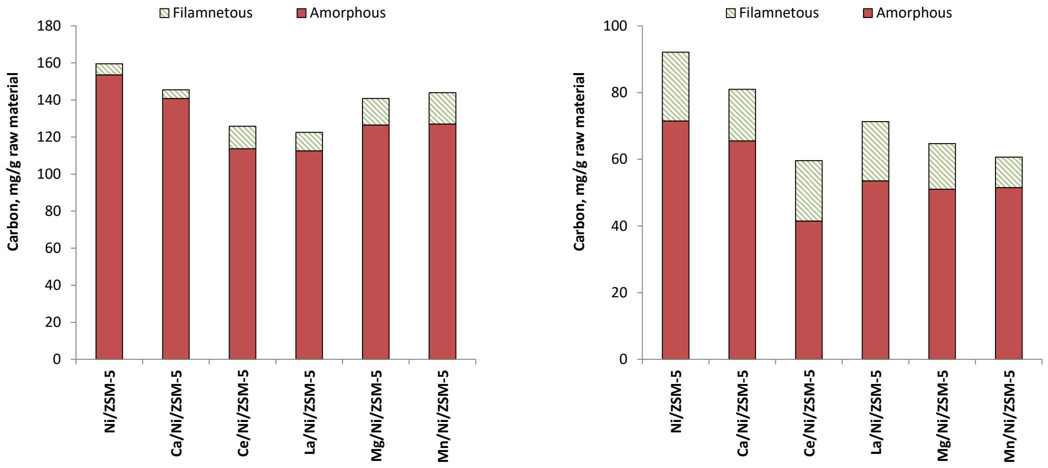
a) b)

Figure 3.34(a,b)
The composition of pyrolysis oil using Me/Ni/ZSM-5 catalysts with
different temperatures (a= 500°C, b= 850°C)

Regarding to the oxygenated compounds, the concentration of carboxylic acid was slightly decreased with the addition of catalyst and further decreased with increasing the reaction temperature. Hence, running the process without catalyst is favoured for the production of these compounds. The highest concentration of carboxylic acid was observed for the thermal pyrolysis at 550 °C. On the other hand, no significant change in the phenol concentration with changing the temperature and catalyst type and Ni/ZSM-5 catalyst produced the maximum yield at 550 °C. The GC- FID results also showed that temperature with second metal prometers could slightly increased the concentration of aldehyde and ketone components in the oil yield. Meanwhile, the same effect was reported on the other compounds in the pyrolysis oil product.

3.5.2.4. Production of carbon nanotubes

Figure 3.35 shows the characterization of carbon deposition on the catalyst surfacce after the experimnet. Filamentos and amorphous carbon were observed on the used catalysts.



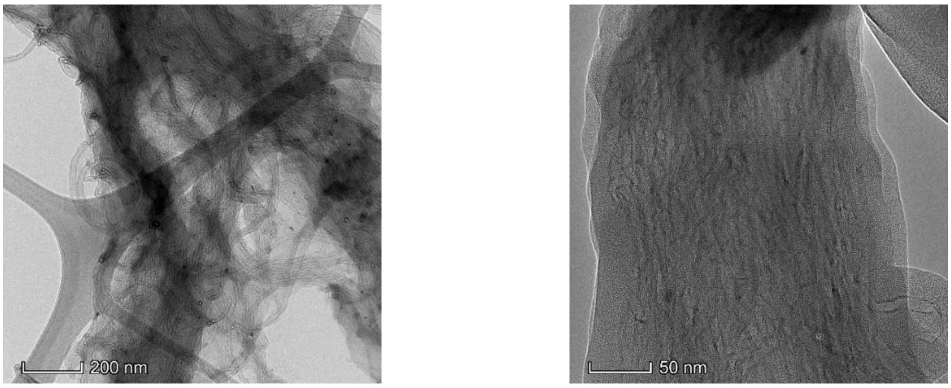
550°C

850°C

Figure 3.35
TPO result of catalyst after pyrolysis

The data showed that the amount of carbon deposition was higher at low temperature 550 °C over the vaious catalysts compared to 850 °C. As it was discussed earlier, the higher temperature favours to the coke reduction from catalyst surface. At low reaction temperature, dominate proportion of amorphous carbon was found on the catalyst surface. Hence, running the expirement at 550 °C is favoured for the formation of amorphous carbon. However, the highest ratio of amorphous carbon at 550 °C was reported over Ni/ZSM-5 catalyst. Increasin the reaction temperature to 850 °C had negative influence on the proportion of amorphous carbon as it is decreased with temperature. On the other hand, temperature had positive effect on the filamentous carbon. Regarding to the influence of second promoters, the obtained results showed that catalyst without promoters produced more carbonouse materials. Moreover, dolomite has a disadvantageous role to the proportion of amorphous carbon at high temperature because lower amount was found at 850 °C. However, the presence of dolomite at high temperature of 850 °C could increase the ratio of filamentous carbon.

The carbonaceous materials obtained from the surface of Ce/Ni/ZSM-5 catalyst are shown in **Figure 3.36.** The TEM images show the formation of CNTs on selected catalyst after the pyrolysis experiments. According to the TEM data, a tubular filamentous carbon was formed over the catalyst surface of Ce/Ni/ZSM-5 catalyst at 850 °C.



Ce/Ni/ZSM-5, 850°C Ce/Ni/ZSM-5, 850°C

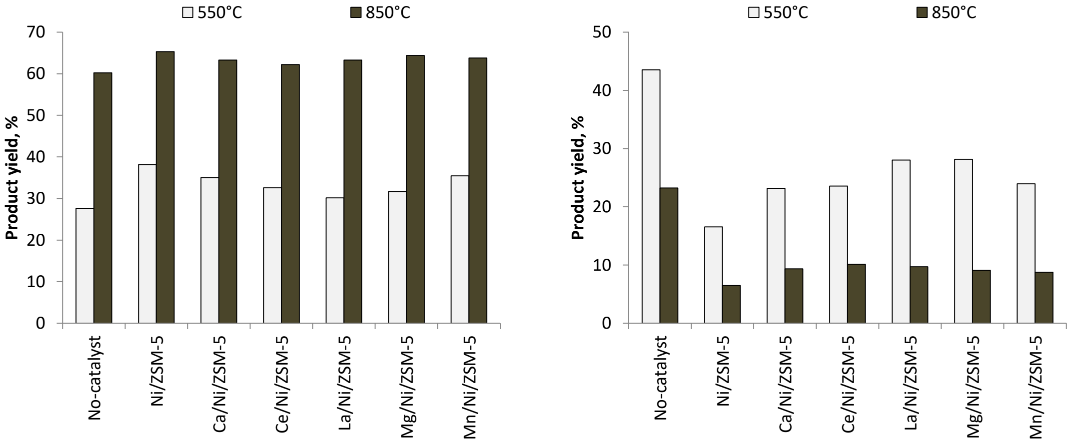
Figure 3.36
TEM images of CNTs on the catalyst surface

3.5.3. Dry reforming of plastics wastes on Ni/Me/ZSM-5 catalyst

In this chapter 0.5 dm^3/h of carbon dioxide flow was used for the gasification of raw materials in the presence and absence of catalyst at 550 and 850 °C.

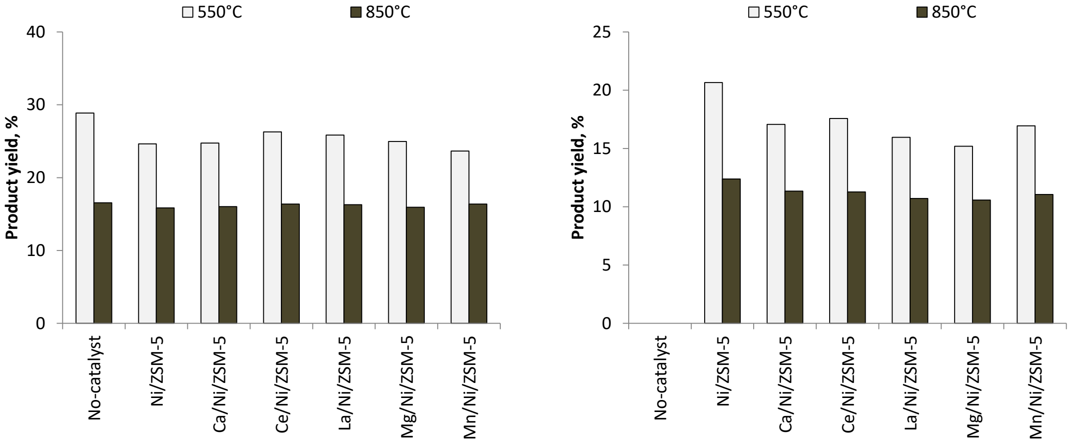
3.5.3.1. Product yields

The obtained products (gases, pyrolysis oil and char) from the exprements are shown in **Figure 3.37**. Based on the obtained data, the addition of catalys had positive effect on the gas yields at both temperatures. Ni/ZSM-5 catalyst showed higher catalytic performance compared to other used catalysts at the two temperatures of 550 and 850 °C. The maximum gas yield was reported in the presence of Ni/ZSM-5 catalyst at 550 and 850 °C which were 38.2 % and 65.3 % respectively. While, no significant change among the other catalysts with second metal promoters. For catalytic pyrolysis, the lowest gas product at 550 °C was obtained with La/Ni/ZSM-5 catalyst, while, Ce/Ni/ZSM-5 catalyst produced the lowest yield at 850 °C. Regardless of catalyst effect, temperature has notable influence on the gas yield especially at high temperature. High temperature promoted the more decomposition reaction due to the more cracking of C-C bond which resulted in more gas in the product yields.



Gases

Pyrolysis oil



Char

Carbon deposition

Figure 3.37
Product yields using different temperatures

On the other hand, temperature and catalyst have opposite influence on the pyrolysis oil yield. The oil product was significantly reduced by introducing the catalyst to the process and further decreased with increasing the temperature. The highest amount of oil product was achieved in the absence of catalyst at low temperature of 550 °C which was 43.5 %. In contrast, the minimum oil yield was found in the presence of Ni/ZSM-5 catalyst at 850 °C which was only 6.5 %. For the catalytic pyrolysis, Mg/Ni/ZSM-5 catalyst at 550 °C had the maximum yield of liquid 28.2 % among the other catalysts. However, the transformation of liquid product into gases was behind the visible reduction of pyrolysis oil at high temperature due to the more cracking of primary decomposition products.

The same tendency was reported for the char yield with rising the reaction temperature to 850 °C as the yield was decreased over the different catalyst and even for the non-catalytic process. The maximum char yield (28.9 %) was produced without catalyst at 550 °C. Generally, product has lower amount of char in comparison to gas and oil yields. This was attributed to the ability of CO_2 for the gasification of char. Meanwhile, the amount of carbon deposition on the catalyst surface was reduced at elevated temperature (850 °C). This is due to the presence of carbon dioxide in the reactor wich resulted in Boudouard reaction.

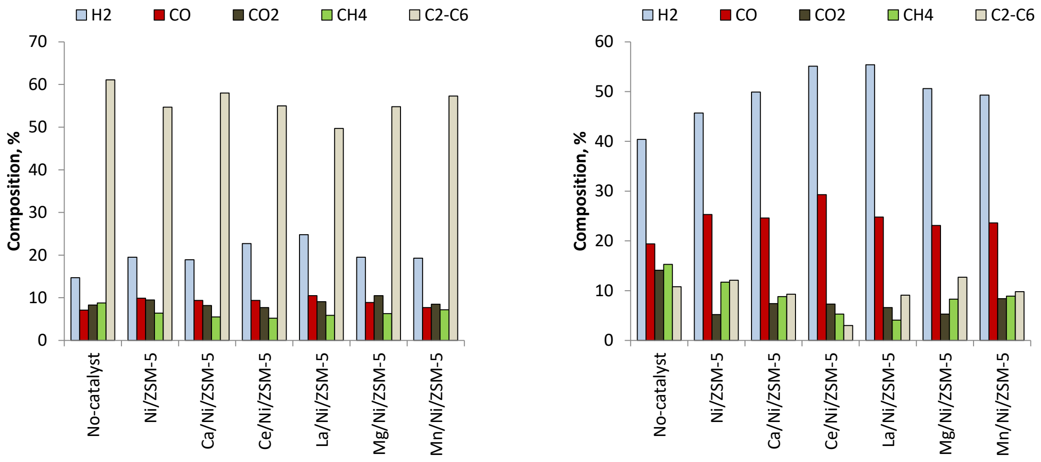
3.5.3.2. Gases

The compositions of gases in the gasification product are represented in **Figure 3.38(a,b)**, which shown that H_2, CO, CO_2, CH_4, linear and brached hydrocarbons (C_2-C_6) were the main components. According to results, the gas compositions were mainly influnced by temperature and catalyst type. Additionally, the CO_2 atmosphere was also affected the gas compositions especially at high temperature (850 °C). The concentration of hydrogen for catalytic process at low temperature was higher compared to thermal process. The addition of catalysts led to increasing of H_2 yield over the various catalysts. The highest H_2 yield was observed in the presence of second metals of Ce and La which were 22.7 % and 24.8 % respectively. While, Ca promoter showed the lowest effect at 550 °C due to the lower H_2 product (18.9 %).

Regarding to CO and CO_2 in the gas composition, catalyst type did not influenced their yields at low reaction temperature as the concentrations were lamost same. The concentration of CO was in the range of 7.1-10.5 %, while it was 7.7-10.5 % in case of CO_2. On the other hand, the concentration of methane was slightly reduced by the presence of catalysts and the maximum CH_4 concnetration (8.8 %) at 550 °C was obtained without catalyst. The data also reported that no significant changes in the concentration of other hydrocarbons (C_2-C_6) with changing the catalyst type at low temperature.

Increasing the reactor temperature to 850 °C resulted in visible effect in the concentration of H_2, CO and other hydrocarbons (C_2-C_6). Regardless of catalyst type, temperature had positive effect on the H_2 yield for the different used catalyst and even for the non-catalytic process. Higher reaction temperature promoted the dry reforming reaction as it needs elevated temperature to occure due to the lowe potential energy of CO_2 [60]. Hence, the more dry reforming reaction *(3.15)*, the more H_2 and CO yields in the product compositions. This was confirmed by the clear decreasing of C_2-C_6 hydrocarbons and CO_2 concentration at 850 °C.

However, the highest H_2 yield was produced over Ce/Ni/ZSM-5 and La/Ni/ZSM-5 catalyst which was 55.1 % and 55.4 % respecively. At the same time, Ce/Ni/ZSM-5 catalyst produced the maximum CO yield at 850 °C. In contrast, a bit increasing was observed in the CH_4 concentration which corresponds to the methanization reaction.

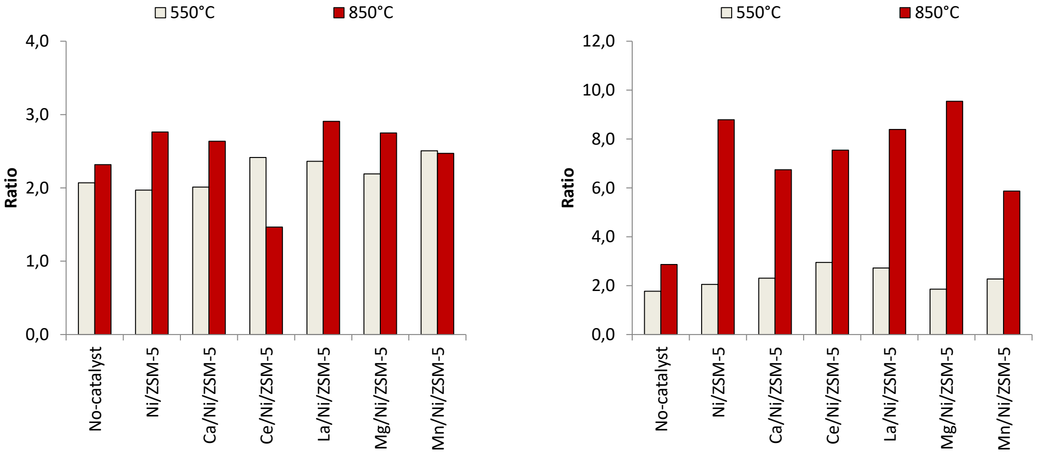


a) b)

Figure 3.38(a,b)
The composition of gases using Me/Ni/ZSM-5 catalysts with different temperatures (a= 550 °C, b= 850°C)

The ratio of H_2/CO and H_2/CO_2 over the different Me/Ni/ZSM-5 catalyst are shown in **Figure 3.39**. The results demonstrated that ratio of H_2/CO for the non-catalytic process did not influence by temperature as the ratio was almost same for both temperatures (2.1). Introducing the Me/Ni/ZSM-5 catalyst to the process at 550 °C led to increasing of H_2/CO ratio except for Ca promoter. The maximum H_2/CO ratio (2.5) was obtained in the presence of Mn/Ni/ZSM-5 catalyst. Furthermore, rising the reactor temperature to 850 °C resulted in different trends. The ratio of H_2/CO was increased in case of Ni/ZSM-5, Ca/Ni/ZSM-5, La /Ni/ZSM-5 and Mg/ Ni/ZSM-5 catalysts but decreased with Ce/Ni/ZSM-5 and Mn/Ni/ZSM-5 catalysts.

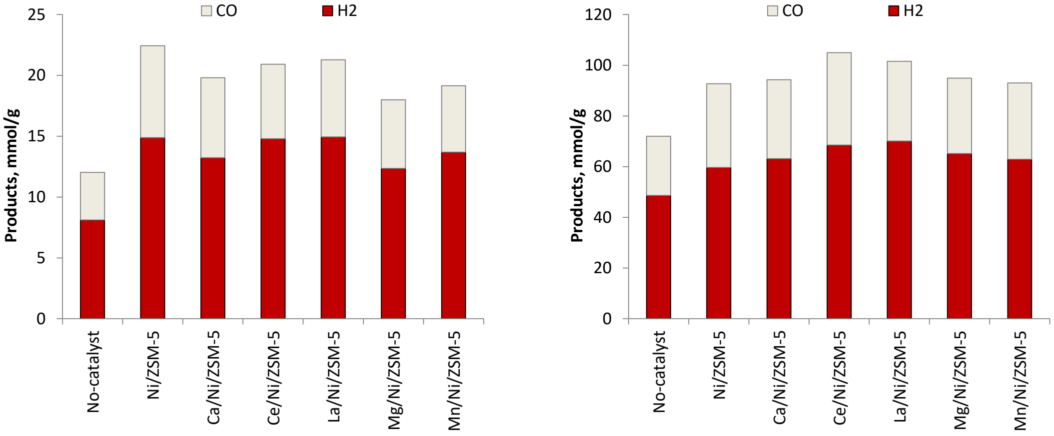
Regarding to the ratio of H_2/CO_2, visible increasing was reported with temperature over the various used catalysts and even for thermal process. At low temperature, the maximum H_2/CO_2 ratio (2.9) was found in the presence of Ce/Ni/ZSM-5 catalyst.while, running the process without catalyst produced the lowest ratio of H_2/CO_2 at 550 °C which was 1.8 on the other hand; catalyst with Mg promoter produced the maximum ratio of H_2/CO_2 at 850 °C which was (9.5).



Ratio of H_2/CO Ratio of H_2/CO_2

Figure 3.39
The ratio of H_2/CO and H_2/CO_2 in gases using Me/Ni/ZSM-5 catalysts with different temperatures

Figure 3.40 illustrats the production of syngas over the different catalyst and various temperatures. Marked increased in the syngas yield was reported over the various used catalysts with rising the temperature to 850 °C. As it mentioned above, high temperature promoting the CO_2 dry reforming reaction and resulted in more syngas product (H_2 and CO). Saad et al. [185] also reported a similar influence of CO_2 addition for the catalytic dry reforming of high density polyethylene at high temperature as the syngas production was improved to 138.81 mmol/g with the presence of catalyst and CO_2 addition.



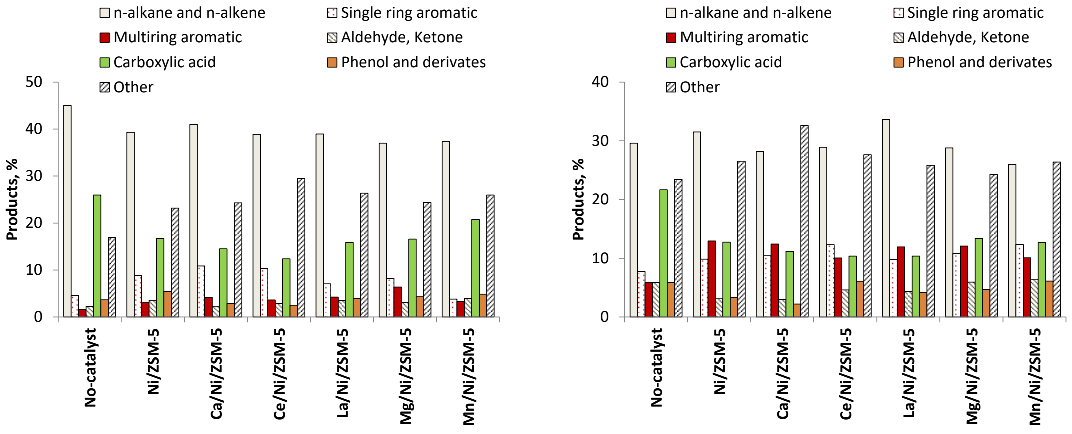
550°C 850°C

Figure 3.40
The yields of hydrogen and carbon-monoxide using Me/Ni/ZSM-5 catalysts with different temperatures

However, the maximum production of syngas was achieved in the presence of Ce/Ni/ZSM-5 and La/Ni/ZSM-5 catalysts which were 105.0 and 101.5 mmol/g respectively. In contrast, Ni/ZSM-5 catalyst produced the maximum syngas at 550 °C with 22.4 mmol/g product yield.

3.5.3.3. Pyrolysis oil

The compositions of oil in the product yield are shown in **Figure 3.41**. N-olefins, n-paraffin, single and multi-ring aromatic, oxygenated and branched compounds were the main compositions of pyrolysis oil. Running the process without catalyst at low temperature of 500 °C produced the maximum concentration of n-paraffine and n-olefine which was 45.0 %. While, introducing the catalysts to the process resulting in slight reduction of n-paraffine and n-olefine concentration. For catalytic process, the concentration of n-paraffine and n-olefine was in the range of 37.0-41.0 % and the maximum yield was found in the presence of Ca/Ni/ZSM-5 catalyst.



550°C 850°C

Figure 3.41
The composition of pyrolysis oil using Me/Ni/ZSM-5 catalysts with different temperatures

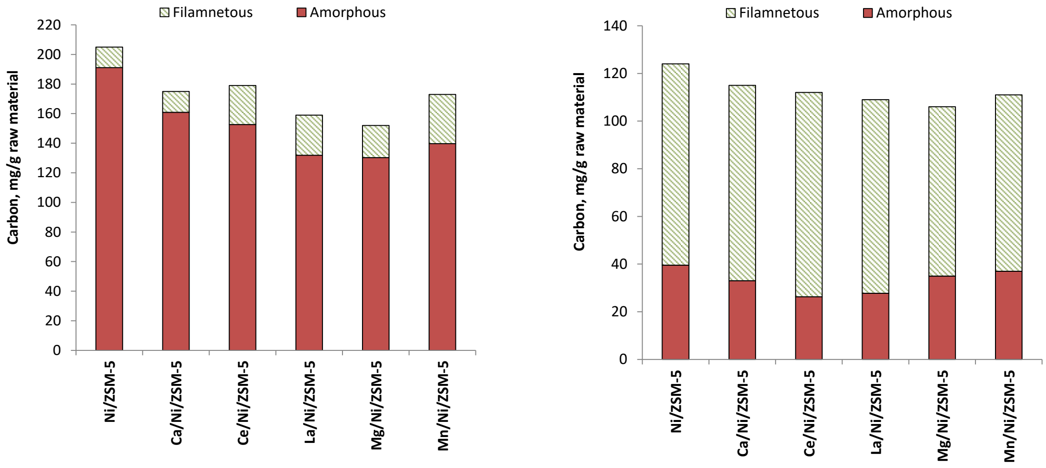
Data showed that the concentration of single ring aromatic in the oil yield was higher than multi-ring aromatic at 550 °C. Moreover, the addition of catalysts promoted the formation of single ring aromatic compounds. However, catalyst with second metals of Ca and Ce produced the maximum yield of single ring aromatic compounds which were 10.9 % and 10.3 % respectively. On the other hand, the maximu concentration of multi-ring aromatic (6.4 %) at low temperature was obtained over Mg/Ni/ZSM-5 catalyst. Regarding to oxygenated compounds in the oil yield, using of catalyst led to decreasing of their concenetration at both temperatures (550 and 850 °C). The maximum concentration of oxygenated compounds was achieved in the absence of catalyst which were 26.0 % and 21.7 % for 550 and 850 °C respectively. On the other hand, the maximum concentration of phenol (5.5 %) in the oil yield at low temperature was reported over Ni/ZSM-5 catalyst.

Increasing the temperature of the reaction to 850 °C resulted in decreasing of n-paraffin and n-olefin concentration over the various bi-metalic catalysts and even for the non-catalytic process. At 850 °C, the highest concentration of n-paraffine and n-olefine was found with La/Ni/ZSM-5 catalyst which was 33.6 %. In contrast, temperature had positive effect on the concentration of single and multi-ring aromatic.

The concentration of multi-ring aromatic was higher than single-ring aromatic at 850 °C. This is due to the ability of Ni/ZSM-5 catalyst for enhancing the aromatization reaction and promoting the more cracking of heavy compounds at high temperature. However, the maximum concentration of multi-ring aromatic (13.0 %) was obtained over Ni/ZSM-5 catalyst, while, catalysts of Ce/Ni/ZSM-5 and Mn/Ni/ZSM-5 produced the highest yield os single-ring aromatic (12.3 %). Rising the temperature led to slight decreasing of oxygenated compounds for both catalytic and non-catalytic processes. On the other hand, no marked changes in concentration of phenol over the catalysts with second promoters of Ca, La and Mg. However, changing the temperature with catalyst did not influenced the concentration of other hydrocarbons in the oil yield.

3.5.3.4. Production of carbon nanotubes

Figure 3.42 shows the TPO results for the selected catalysts after the pyrolysis experiments. The deposited carbon on the catalyst surface was characterized into filamentous and amourphous carbon. It can be seen that the amount of carbon deposition at low temperature of 550 °C was higher than at 850 °C. The reason was attributed to the reduction of coke at high temperature which led to decreasing of carbon deposition at 850 °C. However, the proportion of amorphous carbon was higher than filamentous carbon at 550 °C. The highest ratio of amorphous carbon at low temperature was reported over Ni/ZSM-5 catalyst. On the other hand, increasing of reaction temperature has opposite tendency on the proportion of amorphous carbon as it is decreased with temperature. In contrast, the proportion of filamentous carbon on the catalyst surface was increased with rising the temperature to 850 °C. It is also well shown, that the amount of carboacous materials was lower in the presence of second promoters at both temperatures. The lowest value was found when Mg/Ni/ZSM-5 catalyst had been used in the reactor at both 550 and 850°C. On the other hand, the significant decreasing can be attriduted to the limited formation of amorpohous carbon deposition, because the amount of filamentous carbons was more in case of Me/Ni/ZSMM-5 catalysts, than that of over Ni/ZSM-5.

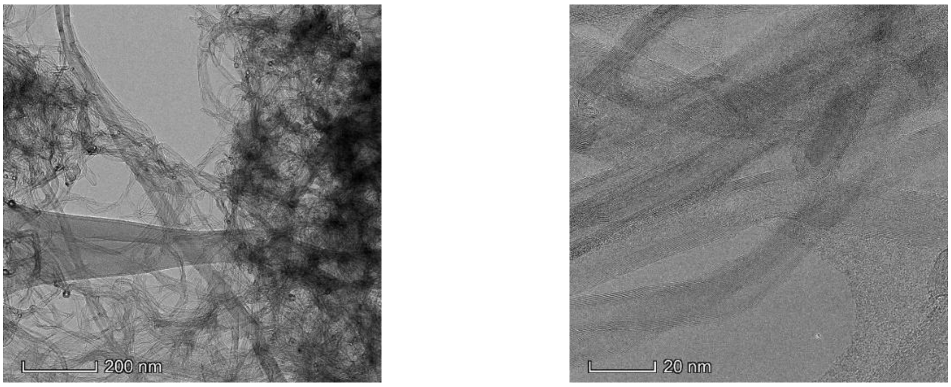


550°C

850°C

Figure 3.42
TPO result of catalyst after pyrolysis

Figure 3.43 shows the TEM images for the CNTs on the catalyst surface of Ce/Ni/ZSM-5 catalyst after the pyrolysis experiments. Figures well demonstrate, that the carbon nanotube has multiwall structure with small diameter (<15mn). As it was before descriebed, the morphology structure was rather filamentous, than amorphous.



Ce/Ni/ZSM-5, 850°C

Ce/Ni/ZSM-5, 850°C

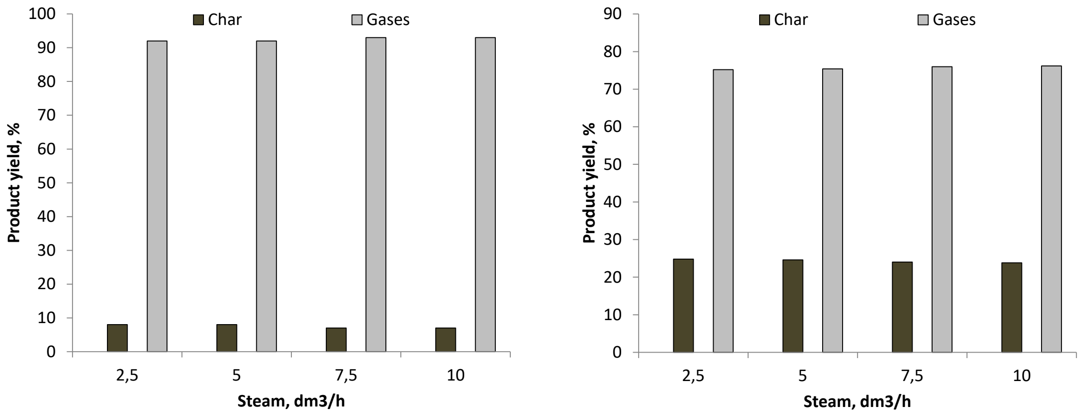
Figure 3.43
TEM images of CNTs on the catalyst surface

3.6. Steam reforming of plastics wastes on Ni/Me/ZSM-5 catalyst

In this chapter the gasification of waste plastic over Ni/ZSM-5, Ce/Ni/ZSM-5 and La/Ni/ZSM-5 catalysts were investigated using two types of reactor (vertical and horizontal). Steam was feed to the reactors at different rate, which are 2.5, 5, 7.5 and 10 g/h. The pyrolysis temperature was set at 550 °C, while the gasification was set at 850 °C. Nitrogen, carbon dioxide was used as reaction atmosphere. Furthermore, dolomite was used for insitu dry reforming.

3.6.1 Investigation the effect of steam rate

Figure 3.44(a,b) shows the product yields (char and gases) for the two reactors (vertical and horizontal) using various steam rate in the presence of Ni/ZSM-5 catalyst. According to the obtained data, the gases products were increased with increasing of steam rate for the both reactors. The highest steam rate of 10 g/h produced the maximum gases yield, which was 93.0 % in case of vertical reactor and 76.2 % in case of horizontal reactor. In contrast, the lowest steam feeding rate resulted in the minimum gas product for the both reactors. On the other hand and regardless of reactor type, increasing of steam rate inside the reactors resulted in lowering of char yields. This is in agreement with the results obtained by [157, 186] who reported that higher ratio of steam feeding led to increasing of gases yields and decreasing of char product. However, the highest char product for the vertical reactor was obtained at lower steam rate of 2.5 g/h which was 8.0 %. The same tendency was reported over the horizontal reactor as the highest amount of char was found at lower steam feeding rate which was 24.8 %.



a) Vertical reactor

b) Horizontal reactor

Figure 3.44(a,b)
Product yields using reactor configurations (nitrogen atmospehere using different steam feed rates)

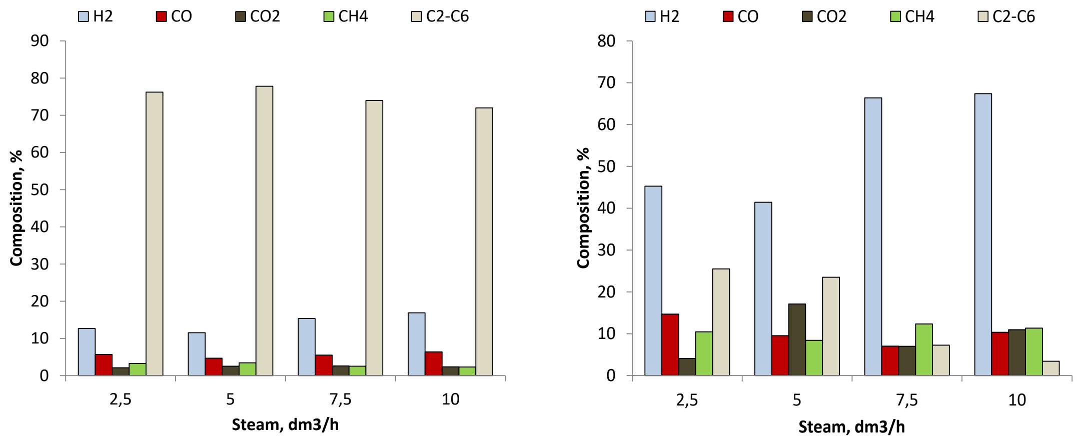
Figure 3.45(a,b) illustrates the composition of gases for the two reactors using various steam rate in the presence of Ni/ZSM-5 catalyst. The pyrolysis-gasification was carried out in inert atmosphere with N_2. It can be seen that hydrogen yield was increased with increasing the steam ratio for the vertical and horizontal reactor. Steam rate of 10 g/h produced the highest yield of hydrogen, which further selected for the catalytic pyrolysis-gasification process. The addition of steam to the process enhanced the production of hydrogen as the steam reacted with carbon in the coke reforming reaction to generate more H_2 product as shown in the equation *(3.16).*

$$C + H_2O \rightarrow CO_2 + H_2 \qquad (3.16)$$

Similar result was reported by Yao et al. [52] who performed the catalytic steam reforming of waste plastic for the production of hydrogen/syngas. The authors observed that increasing of steam rate feeding resulted in more yield of hydrogen product. However, dominate formation of hydrocarbons from C_2 to C_5 was observed for the vertical reactor at all steam ratios. While, opposite tendency was reported for the horizontal reactor, as the hydrogen was the dominate yield. Regarding to CO product in the horizontal reactor, the maximum yield was obtained (14.67 %) was obtained at lower steam ratio of 2.5 g/h. The same trend was found for the other hydrocarbons C_2-C_5, which further decreased with increasing of steam feeding which explain the increasing of hydrogen concentration at higher feeding of steam rate. On the other hand, the increasing of CO_2 concentration for both reactors at high steam feeding rate was attributed to the water gas shift reaction *(3.17).*

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3.17)$$

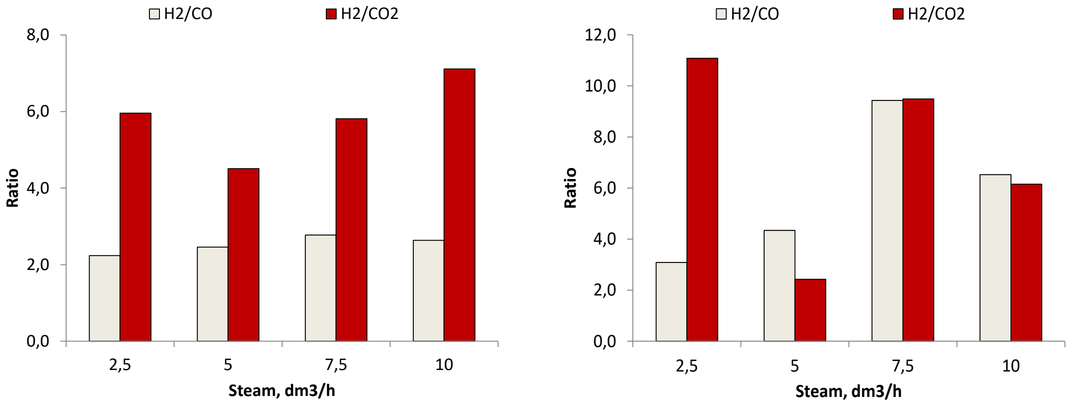
However, steam rate has no effect on the concentration of CH_4 as the yield was almost same for all steam ratios. It was in the range of 10.4 – 12.3 %. On the other hand, the maximum concentration of CO (6.4 %) for the vertical reactor was reported at higher feeding of steam (10 g/h). While no significant change in the concentration of C_2 –C_5.



a) Vertical reactor b) Horizontal reactor

Figure 3.45(a,b)
The compositions of gases at different steam feeding rate

The ratios of H_2/CO and H_2/CO_2 for the vertical and horizontal reactor are shown in **Figure 3.46**. Comparing the data obtained from the two reactors, it can be seen that steam rate did not influenced the ratio of H_2/CO over the vertical reactor as the ratio was almost same over the various steam feeding rate.

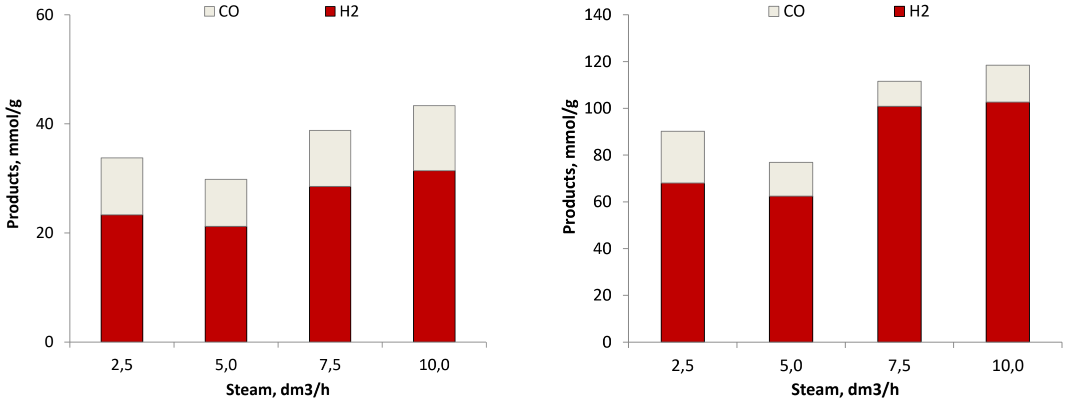


a) Vertical b) Horizontal

Figure 3.46(a,b)
The ratio of H_2/CO and H_2/CO_2 in gases using different steam rates

While, increasing of steam rate had positive effect on the ratio of H_2/CO over the horizontal reactor as it is increased with steam rate. However, the maximum H_2/CO for the both reactors was reported at 7.5 g/h steam feeding rate which was 2.8 and 9.4 respectively. This pehonmena was corresponded to the high product yield of hydrogen at the mentioned steam rate as the steam could promoted the formation of H_2 which led to high ratio of H_2/CO. Regarding to the H_2/CO_2 ratio, the results showed different trends. For the vertical reactor, increasing of steam feeding rate led to increasing of the H_2/CO_2 ratio and steam rate of 10 g/h produced the highest value of H_2/CO_2 ratio (7.1). In contrast, steam feeding had opposite effect on the H_2/CO_2 ratio for the horizontal reactor as the ratio of the H_2/CO_2 was decreased with increasing the steam rate inside the reactor. The highest ratio of the H_2/CO_2 (11.1) for the horizontal reactor was found at the lowest steam feeding rate.

Figure 3.47 illustrats the production of syngas over the different steam rates. Marked increased in the syngas yield was reported for the two reactors (vertical and horizontal) with raising the steam rate of the reaction.



Vertical reactor

Horizontal reactor

Figure 3.47
The yields of hydrogen and carbon-monoxide using different steam rates

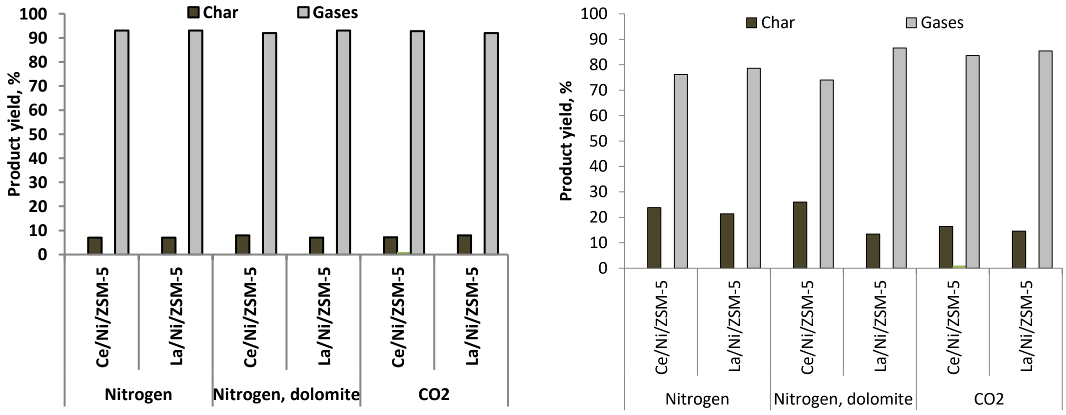
For the vertical reactor, the highest yield of hydrogen and carbon monoxide was obtained with steam feeding of 10 g/h, which were 31.4 and 11.9 mmol/g, respectively. While, the lowest yield was obtained at steam rate of 5 g/h, which were 21.53 and 8.6 mmol/g, respectively. The same trend was reported for the horizontal reactor as the H_2 product was increased with steam rate increasing and steam feeding of 10 g/h produced the highest yield of syngas which was 118.4 mmol/g. Similar data was observed by Yao et al. [52], who performed the catalytic reforming of waste polyethylene for syngas production over different steam rate of 3 and 6 g/h, and various temperatures of 650,750 and 850 °C. They also found that the optimum conditions for syngas yield was achieved with high steam feeding rate of 6 g/h and 850 °C, which was 100.72 mmol/g. As mentioned before, that steam feeding promoted the reforming reactions *(3.18)* which resulted in more hydrogen yield in the product compositions.

$$C_xH_y + H_2O \rightarrow CO + CO_2 + H_2 \tag{3.18}$$

On the other hand, the lowest yield (76.9 mmol/g) was found with steam rate of 5 g/h. Comparing the two reactors, it can be noted that H_2 and CO yields are higher by using the horizontal reactor.

3.6.2 Catalytic steam gasification of waste plastics

Figure 3.48 illustrates the product yields (gases and char) for the catalytic steam gasification for the vertical and horizontal reactor using different atmosphere and catalyst type.

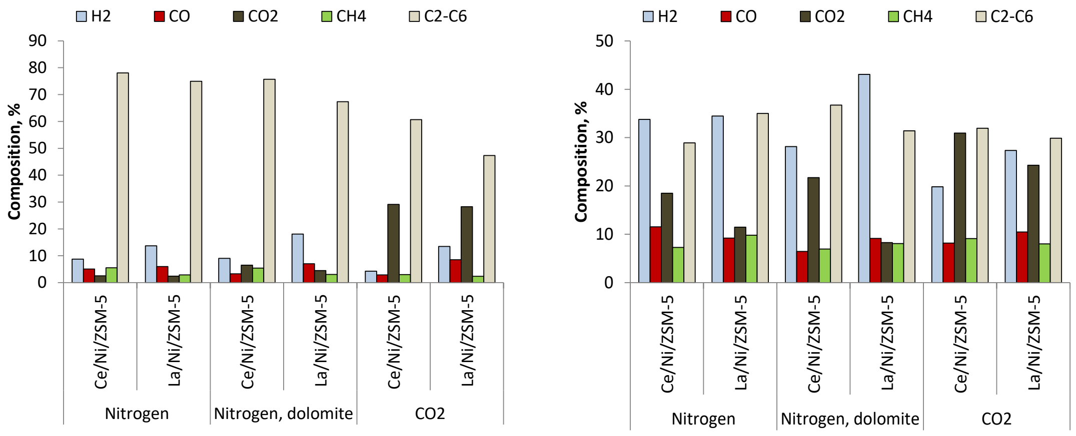


Vertical reactor Horizontal reactor

Figure 3.48
Product yields using reactor configurations (using steam feed rate of 10g/h)

The reported data showed that gas yield for the vertical reactor was almost same for the various atmosphere and catalysts. While, the highest gas product (85.4 -86.6 %) for the horizontal reactor was obtained in the presence of dolomite and CO_2 atmosphere. Regarding to the influence of catalyst type, La/Ni/ZSM-5 produced the maximum gas product for the various atmosphere reaction. This can explain the lowest yield of char in the presence of dolomite for the catalytic process with La/Ni/ZSM-5 catalyst. The reforming of CO_2 from dolomite and dry reforming could enhance the gasification reaction and resulted in more gas product. However, the gas yield for the process with pure nitrogen atmosphere was in the range of 76.2 – 78.6 %.

The gas compositions from catalytic steam gasification using Ce/Ni/ZSM-5 and La/Ni/ZSM-5 catalysts in a horizontal and vertical reactor are shown in **Figure 3.49**. Results demonstrated that atmosphere type have visible effect on the gas yields over the different catalysts.



Vertical reactor Horizontal reactor

Figure 3.49

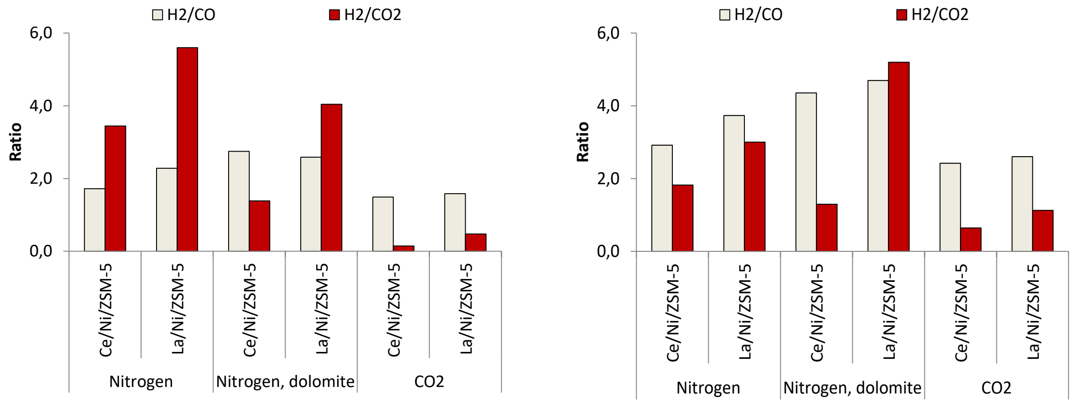
The compositions of gases over the horizontal and vertical reactor

Among the various used atmosphere in the vertical reactor, dolomite for insitu dry reforming generates the maximum hydrogen concentration with product yield of 18.1 % over La/Ni/ZSM-5 catalyst. In the presence of N_2 atmosphere, the concentration of hydrogen was 8.8 and 13.7 % for the Ce/Ni/ZSM-5 and La/Ni/ZSM-5, repectively. Moreover, dominant formation of hydrocarbons ($C_2 – C_6$) was found in case of vertical reactor which explain the low concentration of H_2 and CO in the gas compositions compared to the horizontal reactor. However, the concentration of $C_2 – C_6$ hydrocarbons was in the range of 50 – 78 % for the catalytic gasification. Regarding to CO yield, the maximum concentration was found over La/Ni/ZSM-5 catalyst with CO_2 atmosphere which may attributed to the reverse Boudouard reaction. The concentration of methane was almost same for the both catalysts in the presence of dolomite and N_2 atmosphere.

Regarding to the horizontal reactor, the maximum concentration of hydrogen (43.1 %) was also achieved with dolomite over La/Ni/ZSM-5 catalyst. La/Ni/ZSM-5 showed more catalytic efficiency than Ce/Ni/ZSM-5 catalyst in terms of hydrogen production for the both reactors. In the presence of N_2 atmosphere, the concentration of H_2 was almost same for the both catalysts of Ce/Ni/ZSM-5 and La/Ni/ZSM-5, which was (33.8 - 34.5 %). Regarding to other gas compositions, yields have more CO_2 than CO. The concentration of CO was in the range of 8.2 - 11.6 %, while, the concentration of CO_2 was 8.3 – 30.9 %.

The maximum concentration of methane (9.1 %) was obtained over Ce/Ni/ZSM-5 catalyst. On the other hand, the concentration of other hydrocarbons (C_2-C_6) was relatively lower than with the vertical reactor. However, it was in the range of 28.9 – 35.0 %. Introducing the dolomite to the reaction had positive influence on the hydrogen production over La/Ni/ZSM-5 catalyst as the yield was increased to 43.1 %. While, no significant changes in concentration of other hydrocarbons (C_2-C_5) by changing the reaction atmosphere and catalyst type.

Figure 3.50 shows the ratio of H_2/CO and H_2/CO_2 for the catalytic gasification of waste plastic over the vertical and horizontal reactor in the presence of various reaction atmospheres.

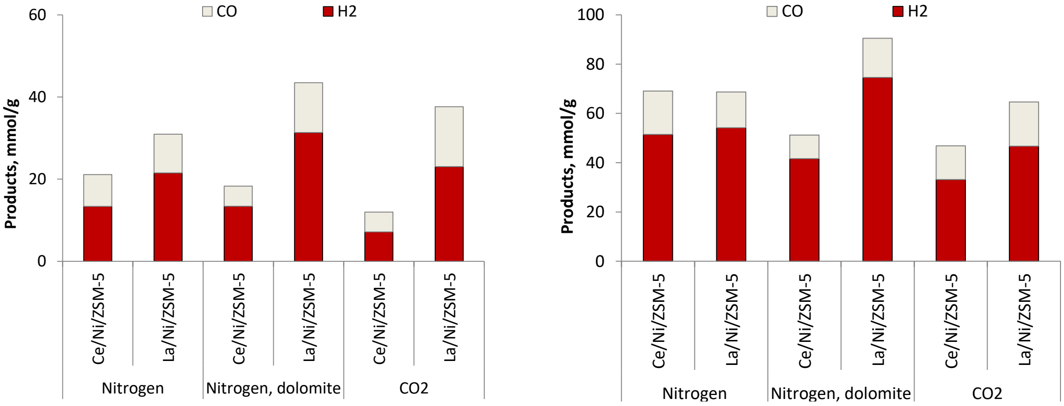


Vertical Horizontal

Figure 3.50
The ratio of H_2/CO and H_2/CO_2 in gases using different cataysts

For both reactors, the data showed that using of dolomite produced the highest H_2/CO ratio which was attributed to the more H_2 product. However, more H_2/CO ratio was found in case of horizontal reactor (4.4 – 4.7) in comparison to the vertical reactor (2.6 – 2.7). In contrast, the lowest H_2/CO ratio was reported in the presence of CO_2 atmosphere. Morover, the results showed that catalyst influence was varied with changing the atmosphere type. On the other hand, the highest ratio of H_2/CO_2 for both reactors was obtained in the pure N_2 and dolomite atmosphere over La/Ni/ZSM-5 catalyst due to the more hydrogen yield and less CO_2. Using of CO_2 as reaction atmosphere resulted in decreasing of H_2/CO_2 ratio due to the more CO_2 in the gas compositions over the vertical and horizontal reactor. It can be seen that the influence of reactor type and reaction atmosphere on the H_2/CO_2 ratio was almost same.

The calculated amount of the syngas (hydrogen and carbon monoxide) in mmol/g for the two reactors is shown in **Figure 3.51.** Regardless of reaction atmosphere type, La/Ni/ZSM-5 catalyst showed higher efficiency than Ce/Ni/ZSM-5 catalyst in terms of hydrogen and CO product. The highest hydrogen value for the vertical and horizontal reactor was obtained in the presence of dolomite and La promoter which was 31.4 and 74.6 mmol/g, respectively. It can be seen that syngas over horizontal reactor are much higher compared to the vertical reactor. As mentioned before that hydrogen and carbon monoxide concentration from the vertical reactor was lower than horizontal reactor due to the high concentration of hydrocarbons (C_2 –C_6) as detected in the GC-TCD. This is the reason for the lower syngas by using the vertical reactor in comparison to the horizontal. However, the minimum amount of syngas was reported over Ce/Ni/ZSM-5 catalyst in the presence of CO_2 reaction atmosphere.



Vertical reactor Horizontal reactor

Figure 3.51
The yields of hydrogen and carbon-monoxide using different catalysts

4. CONCLUSION

In this work, the pyrolysis-gasification of real waste plastic mixture (HDPE, LDPE, PP, and PET) was investigated using vertical and horizontal tubular reactor. The influence of different active metals, catalyst supports, temperatures, and reaction atmosphere on the product yields and compositions were also studied. Furthermore, the selected catalyst was further modified by various second promoters (Ca, Ce, La, Mg, and Mn) and examined for the decomposition reaction of waste plastics. Moreover, the obtained results were compared with the process without catalysts. The product yields (gases, oil, and char) were significantly influenced by the type of catalyst. Gases contained hydrogen, carbon monoxide, cabon dioxide, and methane, branched and non-branched hydrocarbons up to C_5. While, n-olefin, n-paraffin, aromatic, branched and oxygenated compounds were the main compositions of oil product. Among the different catalyst supports (Ni/ZSM-5, Ni/y-zeolite, Ni/natural zeolite, and Ni/β-zeolite), Ni/ZSM-5 showed the highest activity towards gas production and hydrogen yield. In contrast, the maximum oil yield was obtained in the presence of Ni/natural zeolite, and Ni/β-zeolite catalysts. Regarding to the impact of reaction temperature, the results showed that higher temperatures are favouerd for the formation of gases (especially hydrogen and CO). The results also demonstrated that the presence of catalysts at high temperature could increase the concenteration of non-oxygenated compounds in the pyrolysis oil.

Furthermore, first order approach and Arrhenius equation were used to figure out the kinetic paramters for the decomposition reaction over the vaious Me/Ni/ZSM-5 catalysts. The results reported that catalyst behaviors are effected by the different uploaded metals. The apparent activation energy was decreased by introducing the catalyst to the process compared to non-catalystic process. The obtained data showed that the decomposition of PET waste polymer was took place at wide ranges of temperature in the presence of catalyst compared to the thermal pyrolysis. However, while the temperature ranges were wider, the maximum d*m*/d*t* values should be observed at lower temperatures compared to free-catalytic degradation. This practically means that in a pyrolysis plant, the use of catalysts can reduce the energy demand. In general, the activation energy was decreased well by the addition of catalysts.

The influence of different Si/Al ratios of Me/ZSM-5 (Me= Ni, Co, Fe, V, and Zn) is also another important factor which can affect the product yields and compositions from the pyrolysis-gasification reaction. Si/Al ratios of 22.5, 41.9, and 65.5 were tested. It was found that the scission of C-C bonds were mainly effected by the Si/Al ratio and catalyst with high ratio can promoting the more formation of hydrogen and carbon monoxide. Ni/ZSM-5 catalyst showed the best performance compared to other active metals as it is produced the maximum gas yield. While, Zn/Ni/ZSM-5 catalyst produced the highest yield of oil product. Additionally, the Si/Al also affected the char yield as more char was found with higher ratio of Si/Al ratio which was attributed to the Boudouard reaction.

The effect of metal/nickel ratio (0.1, 0.5, and 2.0) on the decomposition of waste (HDPE, LDPE, PP, and PET) was also investigated. Different trends were observed in the gas and oil yields by the application of various Me/Ni ratios. At 0.5 of Me/Ni ratio, Ce/Ni/ZSM-5, La/Ni/ZSM-5, and Mg/Ni/ZSM-5 catalysts showed the better performance, while, Mg/Ni/ZSM-5 and Mn/Ni/ZSM-5 catalysts showed the better properties at Me/Ni ratio of 2.0. In terms of hydrogen and syngas production, Me/Ni ratio of 0.5 was the best compared to other used ratios and Ce/ Ni/ZSM-5 catalyst produced the highest yield of syngas. The results demonstrated that high ratio of second metal led to the blockage of active sites on the catalyst surface due the the more coke formation. Hence, the addition of second promoters on the catalyst should be controlled to avoid such issue.

The reported data also showed that type of atmosphere such as oxygen and carbon dioxide is important factor for the decomposition reaction of waste plastic mixture. Using of oxygen in the carrier gas at different ratios has significant effect on the product yield and compositions. Positive influnce was found in the product yields with increasing of oxygen percentage at high temperature. oxygen has the ability to enhance the production of syngas as a result of partial oxidation reactions. Furthermore, the presence of Me/Ni/ZSM-5 can improve the formation of syngas, especially at high temperature (850 °C). The results also demonstrated that increasing in both the temperature and oxygen concentration contributed to the formation of n-paraffin in the liquid product. While, rising the ratio of oxygen in the carrier gas led to different trends for the CO_2 as it is increased at low temperature (550 °C) and decreased at 850 °C. On the other hand, the CO_2 atmosphere also influences the products yields by increasing the amount of hydrogen. According to the results, using of CO_2 as carrier gas could promoting the more dry reforming reactions at high temperature which led to more syngas product and decreased the carbon deposition on the catalyst surface as well.

On the other hand, the yields and compositions of gases from the gasification process of polyerms were greatly influenced by the incorporation of second metal promoters and the presence of dolomite. The in-situ carbon-dioxide production from dolomite resulted in a marked increase of syngas production and decreased carbon deposition on the catalyst surface at a temperature of 850 °C. Additionally, the catalysts were characterized by using TEM and TPO techniques. Two carbon types of filamentous and amorphous carbon were observed on the catalyst surface. The ratio of filamentous and amorphous carbon was effected by the catalyst and atmosphere type.

Finally, steam was used for the catalytic steam reforming over different reactors (vertical and horizontal). The obtained data showed that the addition of steam promoted the catalytic steam reforming and hydrogen production. In addition, high ratio of steam feeding resulted in more gases in the product compoitions. Comparing both reactors, more syngas yield (H_2 and CO) was found in case of the horizontal reactor. The reported data also showed that steam has negative effect on the char product for the both reactors.

In conclusion, the current study could provide a clear sight about the combination of Me/Ni/ZSM-5 and the role of second promoters in the decomposition reaction of waste plastic (PET, LDPE, HPDE, PP, etc.). Furthermore, the study of different process parameters and various conditions could help in chosing the optimum conditions for better process.

REFRENCES

1. Anuar Sharuddin, S.D., A review on pyrolysis of plastic wastes. Energy Conversion and Management, 2016. 115: p. 308-326.
2. Sogancioglu, M., E. Yel, and G. Ahmetli, Pyrolysis of waste high density polyethylene (HDPE) and low density polyethylene (LDPE) plastics and production of epoxy composites with their pyrolysis chars. Journal of Cleaner Production, 2017. 165: p. 369-381.
3. Rani, K.S., Environmental effects of burning fossil fuels. Journal of Chemical and Pharmaceutical Sciences, 2014. 3: p. 63-67.
4. Khan, M.M., Zaman, K., Irfan, D., Awan, U. Ali, G. Kyophilavong, P., Shahbaz, M., and Naseem I., Triangular relationship among energy consumption, air pollution and water resources in Pakistan. Journal of Cleaner Production, 2016. 112: p. 1375-1385.
5. Zheng, S., H. Yi, and H. Li, The impacts of provincial energy and environmental policies on air pollution control in China. Renewable and Sustainable Energy Reviews, 2015. 49: p. 386-394.
6. Lott, M.C., S. Pye, and P.E. Dodds, Quantifying the co-impacts of energy sector decarbonisation on outdoor air pollution in the United Kingdom. Energy Policy, 2017. 101: p. 42-51.
7. Li, S., K. Feng, and M. Li, Identifying the main contributors of air pollution in Beijing. Journal of Cleaner Production, 2017. 163: p. S359-S365.
8. Zhang, Y., Qu, S., Zhu, G., Zhang, Y. Lu, X., Sabel, C., and Wang, H., Quantifying regional consumption-based health impacts attributable to ambient air pollution in China. Environment International, 2018. 112: p. 100-106.
9. http://ec.europa.eu/eurostata.i.M.overview, I.S.E.s., 2018; 23.12.2019.
11. https://ourworldindata.org/energy, 2019; 23.12.2019.
12. https://www.plasticseurope.org/en/resources/publications/4312-plastics-facts, 2020; 01. 09. 2020.
13. Thompson, R.C., Moore, C., Saal, F., and Swan, S., Plastics, the environment and human health: current consensus and future trends. Philosophical transactions of the Royal Society of London. Series B, Biological sciences, 2009. 364: p. 2153-2166.
14. Cole, M., Microplastics as contaminants in the marine environment: A review. Marine Pollution Bulletin, 2011. 62: p. 2588-2597.
15. Fendall, L.S. and M.A. Sewell, Contributing to marine pollution by washing your face: Microplastics in facial cleansers. Marine Pollution Bulletin, 2009. 58: p. 1225-1228.
16. Teuten, E.L., Rowland, S., Galloway, T. and Thompson, R., Potential for plastics to transport hydrophobic contaminants. Environmental Science & Technology, 2007. 41: p. 7759-7764.
17. Ivar do Sul, J.A. and M.F. Costa, The present and future of microplastic pollution in the marine environment. Environmental Pollution, 2014. 185: p. 352-364.
18. Zarfl, C. and M. Matthies, Are marine plastic particles transport vectors for organic pollutants to the Arctic? Marine Pollution Bulletin, 2010. 60: p. 1810-1814.
19. Chow, C.-F., So, W.-M. W., Cheung, T.-Y., and Yeung, S.-K. D., Plastic waste problem and education for plastic waste management. Chapter in book, Conference proceeding, 2017.
20. Oehlmann, J. Schulte-Oehlmann, U., Kloas, W., Jagnytsch, O., Lutz, I., Kusk, K., Wollenberger, L., Santos, E., Paull, G., Van Look, K., and Tyler, C., A critical

analysis of the biological impacts of plasticizers on wildlife. Philosophical Transactions Of The Royal Society B, 2009. 346: p. 2047-2062.

21. Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Bariaz, A., Jonsson, S., Bjorn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., and Takada, H., Transport and release of chemicals from plastics to the environment and to wildlife. Philosophical Transactions Of The Royal Society B, 2009. 364: p. 2027-2045.
22. Andrady, A.L. and M.A. Neal, Applications and societal benefits of plastics. Philosophical transactions of the Royal Society of London. Series B, Biological sciences, 2009. 364: p. 1977-1984.
23. Briassoulis, D., M. Hiskakis, and E. Babou, Technical specifications for mechanical recycling of agricultural plastic waste. Waste Management, 2013. 33: p. 1516-1530.
24. Eriksson, O., Reich, M.C., Frostell, B., Bjorklund, A., Aseefa, G., Sundqvist, J.-O., Granath, J., Baky, A., and Thyselius, L., Municipal solid waste management from a systems perspective. Journal of Cleaner Production, 2005. 13: p. 241-252.
25. Alabi, O.A., Ologbonjaye, K.I., Awosolu, O., and Alalade, O.E., Public and Environmental Health Effects of Plastic Wastes Disposal: A Review. Journal of Toxicology and Risk Assessment, 2019. 5: p. 5:021.
26. Ragaert, K., L. Delva, and K. Van Geem, Mechanical and chemical recycling of solid plastic waste. Waste Management, 2017. 69: p. 24-58.
27. Martins, F., C. Felgueiras, and M. Smitková, Fossil fuel energy consumption in European countries. Energy Procedia, 2018. 153: p. 107-111.
28. Wanga, J. and G. Cheng, Hydrogen-rich gas production by steam gasification of municipal solid waste (MSW) using NiO supported on modified dolomite. International Journal of Hydrogen Energy, 2012. 37: p. 6503 - 6510.
29. Mackaluso, J.D., The use of syngas derived from biomass and waste products to produce ethanol and hydrogen. Basic Biotechnology eJournal, 2007. 3: p. 98-103.
30. Abatzoglou, N. and C. Fauteux-Lefebvre, Review of catalytic syngas production through steam or dry reforming and partial oxidation of studied liquid compounds. WIREs Energy and Environemnt, 2016. 5: p. 169-187.
31. Wurzel, T., Syngas – The Flexible Solution in a Volatile Feed-stock Market. New Technologies and Alternative Feedstocks in Petrochemistry and Refining DGMK Conference, 2013: p. 9-11.
32. Rostrup-Nielsen, J.R., J. Sehested, and J.K. Nørskov, Hydrogen and synthesis gas by steam and CO_2 reforming, in Advances in Catalysis 2002, Academic Press. p. 65-139.
33. Ausfelder, F. and A. Bazzanella, Chapter 2 - Hydrogen in the chemical industry, in: D. Stolten, B. Emonts (Eds.), Hydrogen Science and Engineering: Materials, Processes, Systems and Technology, Wiley-VCH Verlag GmbH & Co. KGaA, ISBN: 978-3-527-33238-0. 2016: p. 19-40.
34. Vita, A. and C. Italiano, Chapter 4 - Fuel and hydrogen related problems for conventional steam reforming of natural gas, in Current Trends and Future Developments on (Bio-) Membranes, A. Figoli, Y. Li, and A. Basile, Editors. 2020, Elsevier. p. 71-89.
35. Henstra, A.M., Sipma, J., Rinzema, A., and Stams, A.J., Microbiology of synthesis gas fermentation for biofuel production. Current Opinion in Biotechnology, 2007. 18: p. 200-206.
36. Younesi, H., G. Najafpour, and A.R. Mohamed, Ethanol and acetate production from synthesis gas via fermentation processes using anaerobic bacterium, Clostridium ljungdahlii. Biochemical Engineering Journal, 2005. 27: p. 110-119.

37. https://www.sciencedirect.com/topics/engineering/methane-steam-reforming. 20.06.2021
38. Matsumura, Y. and T. Nakamori, Steam reforming of methane over nickel catalysts at low reaction temperature. Applied Catalysis A: General, 2004. 258: p. 107-114.
39. Nieva, M.A., Villaverde, M.M., Monzon, A., Garetto, T.F., and Marchi A.J., Steam-methane reforming at low temperature on nickel-based catalysts. Chemical Engineering Journal, 2014. 235: p. 158-166.
40. Li, D., Y. Nakagawa, and K. Tomishige, Methane reforming to synthesis gas over Ni catalysts modified with noble metals. Applied Catalysis A: General, 2011. 408: p. 1-24.
41. Alvarez-Galvan, C., Melian, M., Ruiz-Mates, L., Eslava, J.L., Navarro,, R.M., Ahmadi, M., Cuenya, B.R., and Fierro, J.L.G., Partial oxidation of methane to syngas over nickel-based catalysts: influence of support type, addition of rhodium, and preparation method. Frontiers in Chemistry, 2019. 7(104).
42. Zhu, T. and M. Flytzani-Stephanopoulos, Catalytic partial oxidation of methane to synthesis gas over Ni–CeO_2. Applied Catalysis A: General, 2001. 208: p. 403-417.
43. Vernon, P.D.F., Green, M.L.H., Cheetham, A.K., and Ashcroft, A.T., Partial oxidation of methane to synthesis gas. Catalysis Letters, 1990. 6: p. 181-186.
44. Asencios, Y.J.O. and E.M. Assaf, Combination of dry reforming and partial oxidation of methane on NiO–MgO–ZrO_2 catalyst: Effect of nickel content. Fuel Processing Technology, 2013. 106: p. 247-252.
45. Badmaev, S.D., Akhmetov, N.O., Belyaev, V.D., Kulikov, A.V., Pechenkin, A.A., Potemkin, D.I., Konishcheva, M.V., Rogozhnikov, V.n., Snytnikov, P.V., and Sobyanin, V.A., Syngas production via partial oxidation of dimethyl ether over Rh/Ceo.75Zro.25O_2 catalyst and its application for SOFC feeding. International Journal of Hydrogen Energy, 2020. 45: p. 26188-26196.
46. Göransson, K., Soderlind, U., He, J., and Zhang, W., Review of syngas production via biomass DFBGs. Renewable and Sustainable Energy Reviews, 2011. 15: p. 482-492.
47. Panepinto, D., Tedesco, V., Brizio, E., and Genon, G., Environmental performances and energy efficiency for MSW gasification treatment. Waste and Biomass Valorization, 2014. 6: p. 123-135.
48. Al-Salem S.M., Antelava, A., Constantinou, A., Manos, G., and Dutta, A., A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). Journal of Environmental Management, 2017. 197: p. 177-198.
49. Al-Zareer, M., I. Dincer, and M.A. Rosen, Production of hydrogen-rich syngas from novel processes for gasification of petroleum cokes and coals. International Journal of Hydrogen Energy, 2020. 45: p. 11577-11592.
50. Zhang, S., Zhu, S., Zhang, H., Liu, X., and Xiong, Y., High quality H_2-rich syngas production from pyrolysis-gasification of biomass and plastic wastes by Ni-Fe @Nanofibers/Porous carbon catalyst. International journal of hydrogen energy, 2019. 44:p. 26193 - 26203.
51. Veses, A., Sanahuja-Parejo, O., Callen, M.S., Murillo, R., and Garcia, T., A combined two-stage process of pyrolysis and catalytic cracking of municipal solid waste for the production of syngas and solid refuse-derived fuels. Waste Management, 2020. 101: p. 171-179.
52. Yao, D., Yang, H., Chen. H., and Williams, P., Investigation of nickel-impregnated zeolite catalysts for hydrogen/syngas production from the catalytic reforming of waste polyethylene. Applied Catalysis B: Environmental, 2018. 227: p. 477-487.

53. Irfan, M., Li, A., Zhang, L., Wang, M., Chen, C. and Khushk, S., Production of hydrogen enriched syngas from municipal solid waste gasification with waste marble powder as a catalyst. International Journal of Hydrogen Energy, 2019. 44: p. 8051-8061.
54. Policella, M., Wang, Z., Bura, K.G., and Gupta, A.K., Characteristics of syngas from pyrolysis and CO_2-assisted gasification of waste tires. Applied Energy, 2019. 254: p. 113678.
55. Wang, Z., Burra, K.G., Li, X., Zhang, M., He, X., Lei, T., and Gupta, A.K., CO_2-assisted gasification of polyethylene terephthalate with focus on syngas evolution and solid yield. Applied Energy, 2020. 276: p. 115508.
56. Déparrois, N., Singh, P., Burra, K.G. and Gupta, A.K., Syngas production from co-pyrolysis and co-gasification of polystyrene and paper with CO_2. Applied Energy, 2019. 246: p. 1-10.
57. Saebea, D., Ruengrit, P., Arpornwichanop, A., Patcharavorachot, Y., Gasification of plastic waste for synthesis gas production. Energy Reports, 2020. 6: p. 202-207.
58. Lin, C.-L., J.-D. Chou, and C.-H. Iu, Effects of second-stage bed materials on hydrogen production in the syngas of a two-stage gasification process. Renewable Energy, 2020. 154: p. 903-912.
59. Saad, J.M. and P.T. Williams, Pyrolysis-catalytic dry (CO_2) reforming of waste plastics for syngas production: Influence of process parameters. Fuel, 2017. 193: p. 7-14.
60. Saad, J.M., M.A. Nahil, and P.T. Williams, Influence of process conditions on syngas production from the thermal processing of waste high density polyethylene. Journal of Analytical and Applied Pyrolysis, 2015. 113: p. 35-40.
61. Nahil, M.A., C. Wu, and P.T. Williams, Influence of metal addition to Ni-based catalysts for the co-production of carbon nanotubes and hydrogen from the thermal processing of waste polypropylene. Fuel Processing Technology, 2015. 130: p. 46-53.
62. Saad, J.M. and P. T.Williams, Manipulating the H2/CO ratio from dry reforming of simulated mixed waste plastics by the addition of steam. Fuel Processing Technology, 2017. 156: p. 331-338.
63. Fakhr Hoseini, S.M. and M. Dastanian, Predicting pyrolysis products of PE, PP, and PET Using NRTL Activity coefficient model. Journal of Chemistry, 2013. 2013: p. 487676.
64. Bridgwater, A.V., Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy, 2012. 38: p. 68-94.
65. Abnisa, F. and W.M.A. Wan Daud, A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. Energy Conversion and Management, 2014. 87: p. 71-85.
66. Europe, A.o.P.M., An analysis of European plastics production, demand and waste data. Belgium: European Association of Plastics Recycling and Recovery Organisations, 2015: p. 1–32.
67. He, M., Xiao, B., Hu, Z., Liu, S. Guo, X. and Luo, S., Syngas production from catalytic gasification of waste polyethylene: Influence of temperature on gas yield and composition. International Journal of Hydrogen Energy, 2009. 34: p. 1342-1348.
68. Alvarez, J., Kumagai,. S., Wu, C., Yoshioka, T., Bilbao, J., Olazar, M., Williams, P.T., Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification. International Journal of Hydrogen Energy, 2014. 39: p. 10883-10891.

69. Irfan, M., Li, A., Zhang, L., Ji, G., Gao, Y., Catalytic gasification of wet municipal solid waste with HfO_2 promoted Ni-CaO catalyst for H_2-rich syngas production. Fuel, 2021. 286: p. 119408.
70. Wu, S.-L., J.-H. Kuo, and M.-Y. Wey, Hydrogen promotion by Co/SiO_2@HZSM-5 core-shell catalyst for syngas from plastic waste gasification: The combination of functional materials. International Journal of Hydrogen Energy, 2019. 44: p. 13480-13489.
71. Yang, R.-X., Wu, S-L., Chuang, K-H., and Wey, M-Y., Co-production of carbon nanotubes and hydrogen from waste plastic gasification in a two-stage fluidized catalytic bed. Renewable Energy, 2020. 159: p. 10-22.
72. Hu, M., Guo,D., Ma, C., Hu, Z., Zhang, B., Xiao, B., Luo, S., and Wang, J., Hydrogen-rich gas production by the gasification of wet MSW (municipal solid waste) coupled with carbon dioxide capture. Energy, 2015. 90: p. 857-863.
73. Guoxin, H. and H. Hao, Hydrogen rich fuel gas production by gasification of wet biomass using a CO_2 sorbent. Biomass and Bioenergy, 2009. 33(5): p. 899-906.
74. Domínguez, A., J.A. Menéndez, and J.J. Pis, Hydrogen rich fuel gas production from the pyrolysis of wet sewage sludge at high temperature. Journal of Analytical and Applied Pyrolysis, 2006. 77: p. 127-132.
75. Chen, G., Jamro, I.A., Samo, S.R., Wenga, T., Balosh, H.A., Yan, B., and Ma, W., Hydrogen-rich syngas production from municipal solid waste gasification through the application of central composite design: An optimization study. International Journal of Hydrogen Energy, 2020. 45: p. 33260-33273.
76. Çepelip ullar, Ö. and A. Pütün, Utilization of two different types of plastic wastes from daily and industrial life. Journal of Selcuk University Natural and Applied Science, 2013: p. 694-706.
77. Jung, S.-H., Chao, M-H., Kang, B-S., and Kim, J-S., Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor. Fuel Processing Technology, 2010. 91: p. 277-284.
78. Williams, P.T. and E.A. Williams, Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock. Journal of Analytical and Applied Pyrolysis, 1999. 51: p. 107-126.
79. Bober, P., Orinak, A., Orinakova, R., Zamostny, P., Ladomersky, J., and Fedorkova, A., Hydrogen production by catalysed pyrolysis of polymer blends. Fuel, 2011. 90: p. 2334-2339.
80. Jan, M.R., J. Shah, and H. Gulab, Catalytic degradation of waste high-density polyethylene into fuel products using $BaCO_3$ as a catalyst. Fuel Processing Technology, 2010. 91: p. 1428-1437.
81. Miskolczi, N., Bartha, L., Deak, G., and Kallo, D., Thermal and thermo-catalytic degradation of high-density polyethylene waste. Journal of Analytical and Applied Pyrolysis, 2004. 72: p. 235-242.
82. Adnan, J. Shah, and M.R. Jan, Thermo-catalytic pyrolysis of polystyrene in the presence of zinc bulk catalysts. Journal of the Taiwan Institute of Chemical Engineers, 2014. 45: p. 2494-2500.
83. Kim, S.-S. and S. Kim, Pyrolysis characteristics of polystyrene and polypropylene in a stirred batch reactor. Chemical Engineering Journal, 2004. 98: p. 53-60.
84. Adrados, A., Marco, I.d., Caballero, B.M., Lopez, A., Laresgoiti, M.F., and Torres, A., Pyrolysis of plastic packaging waste: A comparison of plastic residuals from material recovery facilities with simulated plastic waste. Waste Management, 2012. 32: p. 826-832.

85. HS, F., Elements of chemical reaction engineering. 4th ed. New Jersey: Pearson Education Inc. 2010.
86. Sakata, Y., M.A. Uddin, and A. Muto, Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts. Journal of Analytical and Applied Pyrolysis, 1999. 51: p. 135-155.
87. Abbas-Abadi, M.S., Haghighi, M.N., Yeganeh, H., and G.McDonald, A., Evaluation of pyrolysis process parameters on polypropylene degradation products. Journal of Analytical and Applied Pyrolysis, 2014. 109: p. 272-277.
88. Ahmed, I. and A.K. Gupta, Evolution of syngas from cardboard gasification. Applied Energy, 2009. 86: p. 1732-1740.
89. Garforth, A.A., Lin , Y-H., Sharratt , P.,N., and Dwyer, J., Production of hydrocarbons by catalytic degradation of high density polyethylene in a laboratory fluidised-bed reactor. Applied Catalysis A: General, 1998. 169: p. 331-342.
90. Yan, R., D.T. Liang, and L. Tsen, Case studies—Problem solving in fluidized bed waste fuel incineration. Energy Conversion and Management, 2005. 46: p. 1165-1178.
91. Ruoppolo, G., Ammendola, P., Chirone, R. and Miccio, F., H_2-rich syngas production by fluidized bed gasification of biomass and plastic fuel. Waste Management, 2012. 32: p. 724-732.
92. Mastral, F.J., Esperanza, E., Garcia, P., and Juste, M., Pyrolysis of high-density polyethylene in a fluidised bed reactor. Influence of the temperature and residence time. Journal of Analytical and Applied Pyrolysis, 2002. 63: p. 1-15.
93. Murata, K., K. Sato, and Y. Sakata, Effect of pressure on thermal degradation of polyethylene. Journal of Analytical and Applied Pyrolysis, 2004. 71: p. 569-589.
94. Ludlow-Palafox, C. and H.A. Chase, Microwave-induced pyrolysis of plastic wastes. Industrial & Engineering Chemistry Research, 2001. 40: p. 4749-4756.
95. Mastral, F.J., Esperanza, E., Berrueco, C., Juste, M., and Ceamanos, J., Fluidized bed thermal degradation products of HDPE in an inert atmosphere and in air–nitrogen mixtures. Journal of Analytical and Applied Pyrolysis, 2003. 70: p. 1-17.
96. Kyaw, K.T. and C.S.S. Hmwe, Effect of various catalysts on fuel oil pyrolysis process of mixed plastic wastes. International Journal of Advances in Engineering & Technology, 2015. 8: p. 794-802.
97. Saad, J.M. and P.T. Williams, Catalytic dry reforming of waste plastics from different waste treatment plants for production of synthesis gases. Waste Management, 2016. 58: p. 214-220.
98. Yao, D., Wu, C., Yang, H., Zhang, Y., Nahil, M.A., Chen, Y., Williams, P.T., and Chen, H., Co-production of hydrogen and carbon nanotubes from catalytic pyrolysis of waste plastics on Ni-Fe bimetallic catalyst. Energy Conversion and Management, 2017. 148: p. 692-700.
99. Sebestyén, Z., Bartra-Rajnai, E., Bozi, J., Blazso, M., Jakab, E., Miskolczi, N., Soja, J., and Czegeny, Zs., Thermo-catalytic pyrolysis of biomass and plastic mixtures using HZSM-5. Applied Energy, 2017. 207: p. 114-122.
100. Sriningsih, W., Saerodji, M.G., Trisunaryanti, W., Armunanto, R., and Falah, L.L., Fuel Production from LDPE Plastic Waste over Natural Zeolite Supported Ni, Ni-Mo, Co and Co-Mo Metals. Procedia Environmental Sciences, 2014. 20: p. 215-224.
101. Zhang, Y. and P.T. Williams, Carbon nanotubes and hydrogen production from the pyrolysis catalysis or catalytic-steam reforming of waste tyres. Journal of Analytical and Applied Pyrolysis, 2016. 122: p. 490-501.

102. Escola, J.M., Aquado, J., Serrano, D.P., Garcia, A., Peral, A., Briones, L., Calvo, R., and Fernandez, E., Catalytic hydroreforming of the polyethylene thermal cracking oil over Ni supported hierarchical zeolites and mesostructured aluminosilicates. Applied Catalysis B: Environmental, 2011. 106: p. 405-415.
103. Xue, Y., P. Johnston, and X. Bai, Effect of catalyst contact mode and gas atmosphere during catalytic pyrolysis of waste plastics. Energy Conversion and Management, 2017. 142: p. 441-451.
104. Hu, Z., E. Jiang, and X. Ma, The effect of oxygen carrier content and temperature on chemical looping gasification of microalgae for syngas production. Journal of the Energy Institute, 2019. 92: p. 474-487.
105. Rapagnà, S., Jand, N., Kiennemann, A., and Foscolo, P.U., Steam-gasification of biomass in a fluidised-bed of olivine particles. Biomass and Bioenergy, 2000. 19: p. 187-197.
106. Al-asadi, M., N. Miskolczi, and Z. Eller, Pyrolysis-gasification of wastes plastics for syngas production using metal modified zeolite catalysts under different ratio of nitrogen/oxygen. Journal of Cleaner Production, 2020. 271: p. 122186.
107. Grause, G., Matsumoto, S., Kameda, T., and Yoshioka, T., Pyrolysis of mixed plastics in a fluidized bed of hard burnt lime. Industrial & Engineering Chemistry Research, 2011. 50: p. 5459-5466.
108. Lopez, G., Erkiaga, A., Amutio, M., Alvarez, J., and Barbarias, I., Steam gasification of waste plastics in a conical spouted bed reactor. The 14th International Conference on Fluidization – From Fundamentals to Products, 2013.
109. Wu, C. and P.T. Williams, Ni/CeO_2/ZSM-5 catalysts for the production of hydrogen from the pyrolysis–gasification of polypropylene. International Journal of Hydrogen Energy, 2009. 34: p. 6242-6252.
110. Encinar, J.M. and J.F. González, Pyrolysis of synthetic polymers and plastic wastes. Kinetic study. Fuel Processing Technology, 2008. 89: p. 678-686.
111. Aboulkas, A., K. El Harfi, and A. El Bouadili, Non-isothermal kinetic studies on co-processing of olive residue and polypropylene. Energy Conversion and Management, 2008. 49: p. 3666-3671.
112. Zhaosheng, Y., M. Xiaoqian, and L. Ao, Thermogravimetric analysis of rice and wheat straw catalytic combustion in air- and oxygen-enriched atmospheres. Energy Conversion and Management, 2009. 50: p. 561-566.
113. Zhou, L., T. Luo, and Q. Huang, Co-pyrolysis characteristics and kinetics of coal and plastic blends. Energy Conversion and Management, 2009. 50: p. 705-710.
114. Gao, N., Quan, C., Eller, Z., Toth, O., Miskloczi, N., and Al-asadi, M., Thermo-catalytic pyrolysis of wastes using bimetal-modified ZSM-5 catalyst: investigation of the reaction kinetic parameters. Energy Research, 2021.
115. Çepelioğullar, Ö., H. Haykırı-Açma, and S. Yaman, Kinetic modelling of RDF pyrolysis: Model-fitting and model-free approaches. Waste Management, 2016. 48: p. 275-284.
116. Tondl, G., L. Bonell, and C. Pfeifer, Thermogravimetric analysis and kinetic study of marine plastic litter. Marine Pollution Bulletin, 2018. 133: p. 472-477.
117. Gao, N., A.T. Sipra, and C. Quan, Thermogravimetric analysis and pyrolysis product characterization of municipal solid waste using sludge fly ash as additive. Fuel, 2020. 281: p. 118572.
118. Özsin, G. and A.E. Pütün, TGA/MS/FT-IR study for kinetic evaluation and evolved gas analysis of a biomass/PVC co-pyrolysis process. Energy Conversion and Management, 2019. 182: p. 143-153.

119. Fong, M.J.B., Loy, A.C.M., Chin, B.L.F., Lam, M.K., Yusup, S., and Jawad, Z.A., Catalytic pyrolysis of Chlorella vulgaris: Kinetic and thermodynamic analysis. Bioresource Technology, 2019. 289: p. 121689.
120. Alam, M., Bhavanam, A., Jana, A., Viroja, J.K.S., and Peela, N.R., Co-pyrolysis of bamboo sawdust and plastic: Synergistic effects and kinetics. Renewable Energy, 2020. 149: p. 1133-1145.
121. Mishra, R.K., A. Sahoo, and K. Mohanty, Pyrolysis kinetics and synergistic effect in co-pyrolysis of samanea saman seeds and polyethylene terephthalate using thermogravimetric analyser. Bioresource Technology, 2019. 289: p. 121608.
122. Schubert, T., Lechleitner, A., Lehner, M., and Hofer, W., 4-Lump kinetic model of the co-pyrolysis of LDPE and a heavy petroleum fraction. Fuel, 2020. 262: p. 116597.
123. Till, Z., Varga, T., Soja, J., Miskolczi, N., and Chovan, T., Kinetic identification of plastic waste pyrolysis on zeolite-based catalysts. Energy Conversion and Management, 2018. 173: p. 320-330.
124. Till, Z., Varga, T., Soja, J., Miskolczi, N., and Chovan, T., Kinetic modeling of plastic waste pyrolysis in a laboratory scale two-stage reactor, 2018. p. 349-354.
125. Navarro, M.V., Lopez, J.M., Veses, A., Callen, M.S., and Garcia, T., Kinetic study for the co-pyrolysis of lignocellulosic biomass and plastics using the distributed activation energy model. Energy, 2018. 165: p. 731-742.
126. Qiao, Y., Xu, F., Xu, S., Yang, D., Wang, B., Ming, X., Hao, J. and Tian, Y., Pyrolysis characteristics and kinetics of typical municipal solid waste components and their mixture: Analytical TG-FTIR study. Energy & Fuels, 2018. 32: p. 10801-10812.
127. Chhabra, V., S. Bhattacharya, and Y. Shastri, Pyrolysis of mixed municipal solid waste: Characterisation, interaction effect and kinetic modelling using the thermogravimetric approach. Waste Management, 2019. 90: p. 152-167.
128. Menares, T., Herrera, J., Romero, R., Osorio, P., and Arteaga-Perez L.E., Waste tires pyrolysis kinetics and reaction mechanisms explained by TGA and Py-GC/MS under kinetically-controlled regime. Waste Management, 2020. 102: p. 21-29.
129. Gou, X., Zhao, X., Singh, S., and Qiao, D., Tri-pyrolysis: A thermo-kinetic characterisation of polyethylene, cornstalk, and anthracite coal using TGA-FTIR analysis. Fuel, 2019. 252: p. 393-402.
130. Giwa, A.S., Xu, H., Wu, J., Chang, F., Zhang, X., and Jin, Z., Sustainable recycling of residues from the food waste (FW) composting plant via pyrolysis: Thermal characterization and kinetic studies. Journal of Cleaner Production, 2018. 180: p. 43-49.
131. Aguado, R., Olazar, M., Jose, M.J.S., Gaisan, B., and Bilbao, J., Wax formation in the pyrolysis of polyolefins in a conical spouted bed reactor. Energy & Fuels, 2002. 16: p. 1429-1437.
132. Al-Salem, S.M. and P. Lettieri, Kinetic study of high density polyethylene (HDPE) pyrolysis. Chemical Engineering Research and Design, 2010. 88: p. 1599-1606.
133. Williams, E.A. and P.T. Williams, The pyrolysis of individual plastics and a plastic mixture in a fixed bed reactor. Journal of Chemical Technology & Biotechnology, 1997. 70: p. 9–20.
134. Wei, T.-T., Wu, K-J., Lee, S-L., and Lin, Y-H., Chemical recycling of post-consumer polymer waste over fluidizing cracking catalysts for producing chemicals and hydrocarbon fuels. Resources, Conservation and Recycling, 2010. 54: p. 952-961.

135. López, A., Marco, I.de, Caballero, B.M., Laresgoiti, M.F., Aranzabal, A., Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and red mud. Applied Catalysis B: Environmental, 2011. 104: p. 211-219.
136. Marcilla, A., Garcia-Quesada, J.C., Sanchez, S., and Ruiz, R., Study of the catalytic pyrolysis behaviour of polyethylene–polypropylene mixtures. Journal of Analytical and Applied Pyrolysis, 2005. 74: p. 387-392.
137. Pinto, F., Costa, P., Gulyurtlu, I. and Cabrita, I., Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield. Journal of Analytical and Applied Pyrolysis, 1999. 51: p. 39-55.
138. Eswaramoorthi, M., Venkateshan, T., Kumaran, M.B., Gejendhiran, S., Review of plastic waste management by pyrolysis process with Indian perspective. International Journal for Research in Applied Science & Engineering Technology, 2016. 4: p. 514-517.
139. Wong, S.L., Ngadi, N., Abdullah, T.A.T., and Inuwa, I.M., Current state and future prospects of plastic waste as source of fuel: A review. Renewable and Sustainable Energy Reviews, 2015. 50: p. 1167-1180.
140. B, P., Biomass gasification and pyrolysis. Practical design and theory. USA: Elsevier Inc, 2010.
141. Onwudili, J.A., N. Insura, and P.T. Williams, Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time. Journal of Analytical and Applied Pyrolysis, 2009. 86: p. 293-303.
142. Namioka, T., Saito, A., Ionue, Y., Park, Y., Min, T-J., Roh, S-A., and Yoshikawa, K., Hydrogen-rich gas production from waste plastics by pyrolysis and low-temperature steam reforming over a ruthenium catalyst. Applied Energy, 2011. 88(6): p. 2019-2026.
143. Lopez-Urionabarrenechea, A., Marco, I.de, Caballero, B.M., Laresgoiti, M.F. and Adrados, A., Catalytic stepwise pyrolysis of packaging plastic waste. Journal of Analytical and Applied Pyrolysis, 2012. 96: p. 54-62.
144. Wang, J., Cheng, G., You, Y., Xiao, B., Liu, S., He, P., Guo, D., Guo, X., and Zhang, G., Hydrogen-rich gas production by steam gasification of municipal solid waste (MSW) using NiO supported on modified dolomite. International Journal of Hydrogen Energy, 2012. 37(8): p. 6503-6510.
145. Bourke, J., Manely-Harris, M., Fushimi, C., Dowaki,K., Nunoura, T., and Antal, J., Do all carbonized charcoals have the same chemical structure? 2. A model of the chemical structure of carbonized charcoal. Industrial & Engineering Chemistry Research, 2007. 46: p. 5954-5967.
146. Y, F., A. A, and M. JA, Microwave heating applied to pyrolysis. Advances in induction and microwave heating of mineral and organic materials. Spain: InTech, 2011.
147. Jamradloedluk, J. and C. Lertsatitthanakorn, Characterization and utilization of char derived from fast pyrolysis of plastic wastes. Procedia Engineering, 2014. 69: p. 1437-1442.
148. Ahmad, I., Khan, M.I., Khan, H., Ishaq,.M., Khan, R., Gul, K., and Ahmed, W., Pyrolysis of HDPE into fuel like products: Evaluating catalytic performance of plain and metal oxides impregnated waste brick kiln dust. Journal of Analytical and Applied Pyrolysis, 2017. 124: p. 195-203.
149. Das, P. and P. Tiwari, The effect of slow pyrolysis on the conversion of packaging waste plastics (PE and PP) into fuel. Waste Management, 2018. 79: p. 615-624.

150. Mullen, C.A., C. Dorado, and A.A. Boateng, Catalytic co-pyrolysis of switchgrass and polyethylene over HZSM-5: Catalyst deactivation and coke formation. Journal of Analytical and Applied Pyrolysis, 2018. 129: p. 195-203.
151. Kumagai, S., Hasegawa, I., Grasue, G., Kameda, T., and Yoshioka, T., Thermal decomposition of individual and mixed plastics in the presence of CaO or $Ca(OH)_2$. Journal of Analytical and Applied Pyrolysis, 2015. 113: p. 584-590.
152. Brachi, P., Chirone, R., Miccio, F., Miccio, M., Picarelli, A., and Ruoppolo, G., Fluidized bed co-gasification of biomass and polymeric wastes for a flexible end-use of the syngas: Focus on bio-methanol. Fuel, 2014. 128: p. 88-98.
153. Wu, C., Nahil, M.A., Miskolczi, N., Huang, J., and Williams, P.T., Production and application of carbon nanotubes, as a co-product of hydrogen from the pyrolysis-catalytic reforming of waste plastic. Process Safety and Environmental Protection, 2016. 103: p. 107-114.
154. Gong, J., Yao, K., Liu, J., Chen, X., Jiang, Z., Mijowska, E., and Tang, T., Catalytic conversion of linear low density polyethylene into carbon nanomaterials under the combined catalysis of Ni_2O_3 and poly(vinyl chloride). Chemical Engineering Journal, 2013. 215-216: p. 339-347.
155. Liu, J., Jiang, Z., Yu, H., and Tang, T., Catalytic pyrolysis of polypropylene to synthesize carbon nanotubes and hydrogen through a two-stage process. Polymer Degradation and Stability, 2011. 96: p. 1711-1719.
156. Bajad, G., Vijayakumar, R.P., Rakunde, P., Hate, A., and Bhade, M., Processing of mixed-plastic waste to fuel oil, carbon nanotubes and hydrogen using multi–core reactor. Chemical Engineering and Processing: Process Intensification, 2017. 121: p. 205-214.
157. Acomb, J.C., C. Wu, and P.T. Williams, Control of steam input to the pyrolysis-gasification of waste plastics for improved production of hydrogen or carbon nanotubes. Applied Catalysis B: Environmental, 2014. 147: p. 571-584.
158. Acomb, J.C., C. Wu, and P.T. Williams, Effect of growth temperature and feedstock:catalyst ratio on the production of carbon nanotubes and hydrogen from the pyrolysis of waste plastics. Journal of Analytical and Applied Pyrolysis, 2015. 113: p. 231-238.
159. Mishra, N., Das, G., Ansaldo, A., Genovese, A., Malerba, M., Povia, M., Ricci, M., Fabrizio, E., Zitti, E., Sharon, M., and Sharon, M., Pyrolysis of waste polypropylene for the synthesis of carbon nanotubes. Journal of Analytical and Applied Pyrolysis, 2012. 94: p. 91-98.
160. Wang, G., Wang, H., Tang, Z., Li, W., and Bai, J., Simultaneous production of hydrogen and multi-walled carbon nanotubes by ethanol decomposition over Ni/Al_2O_3 catalysts. Applied Catalysis B: Environmental, 2009. 88: p. 142-151.
161. Seelam, P.K., Huuhtanen, M., Sapi, A., Szabo, M., Kordas, K., Turpeinen, E., and Toth G., CNT-based catalysts for H_2 production by ethanol reforming. International Journal of Hydrogen Energy, 2010. 35: p. 12588-12595.
162. Ball, M. and M. Weeda, The hydrogen economy - vision or reality. International Journal of Hydrogen Energy, 2015. 40 p. 7903 -7919.
163. Weissman, R., Recycling of mixed plastic waste by the Texaco gasification process. Chemical Aspects of Plastics Recycling, The Royal Society of Chemistry Information Services, Cambridge., 1997.
164. Materazzi, M., Taylor, R., Cozens, P., Manson-Whitton, C., Production of BioSNG from waste derived syngas: Pilot plant operation and preliminary assessment. Waste Management, 2018. 79: p. 752-762.

165. Donatelli, A., P. Iovane, and A. Molino, High energy syngas production by waste tyres steam gasification in a rotary kiln pilot plant. Experimental and numerical investigations. Fuel, 2010. 89: p. 2721-2728.
166. Huynh, C.V. and S.-C. Kong, Performance characteristics of a pilot-scale biomass gasifier using oxygen-enriched air and steam. Fuel, 2013. 103: p. 987-996.
167. Arena, U. and F. Di Gregorio, Gasification of a solid recovered fuel in a pilot scale fluidized bed reactor. Fuel, 2014. 117: p. 528-536.
168. Pinto, F., Andre, R.N., Carolino, C., Miranda, M., Abelha, P., Direito, D., Dohrup, J., Sorensen, H.R. and Girio, F., Effects of experimental conditions and of addition of natural minerals on syngas production from lignin by oxy-gasification: Comparison of bench- and pilot scale gasification. Fuel, 2015. 140: p. 62-72.
169. Campoy, M., Gomez-Barea, A., Ollero, P., and Nilsson, S., Gasification of wastes in a pilot fluidized bed gasifier. Fuel Processing Technology, 2014. 121: p. 63-69.
170. Begum, S., Rasul, M.G., Cork, D., and Akbar, D., An Experimental investigation of solid waste gasification using a large pilot scale waste to energy plant. Procedia Engineering, 2014. 90: p. 718-724.
171. Jeong, Y.-S., Choi, Y-K., Kang, B-S., Ryu, J-H., Kim, H-S., Kang, M-S., Ryu, L-H., and Kim, J-S., Lab-scale and pilot-scale two-stage gasification of biomass using active carbon for production of hydrogen-rich and low-tar producer gas. Fuel Processing Technology, 2020. 198: p. 106240.
172. Monir, M.U., Aziz, A.A., Kristanti, R.A., and Yousuf, A., Syngas production from co-gasification of forest residue and charcoal in a pilot scale downdraft reactor. Waste and Biomass Valorization, 2020. 11: p. 635-651.
173. Schweitzer, D., Beirow, M., Gredinger, A., Armbrust, N., Waizmann, G., Dieter, H., and Scheffkecht, G., Pilot-scale demonstration of oxy-ser steam gasification: production of syngas with pre-combustion CO_2 capture. Energy Procedia, 2016. 86: p. 56-68.
174. Brems, A., Dewil, R., Baeyens, J., and Zhang, R., Gasification of plastic waste as waste-to-energy or waste-to-syngas recovery route. Natural Science, 2013. 5: p. 695-704.
175. Hirm, G., Generating syngas from plastic wastes. Research project, Germany: p. 0327490A.
176. Qureshi, M.S., Oasmaa, A., Pihkola, H., Deviatkin, I., Tenhunen, A., Mannila, J., Minkkinen, H., Pohjakallio, M., Laine-Ylijoki, J., Pyrolysis of plastic waste: Opportunities and challenges. Journal of Analytical and Applied Pyrolysis, 2020: p. 104804.
177. Sharma, S.D., Dolan, M., Park, D., Morpeth, L., Llyushechkin, A., Mclennan, K., Harris, D.J., and Thambimuthu, K.V., A critical review of syngas cleaning technologies — fundamental limitations and practical problems. Powder Technology, 2008. 180: p. 115-121.
178. http://www.legislation.gov.uk/ukpga/2008/27/pdfs/ukpga_20080027,2018; 12.05.2020.
179. Al-asadi, M. and N. Miskolczi, High temperature pyrolysis of municipal plastic waste using Me/Ni/ZSM-5 Catalysts: The effect of metal/nickel ratio. Energies, 2020. 13: p. 1284.
180. Al-asadi, M. and N. Miskolczi, Pyrolysis of polyethylene terephthalate containing real waste plastics using Ni loaded zeolite catalysts. IOP Conference Series: Earth and Environmental Science, 2018. 154: p. 012021.

181. Al-asadi, M., L. Gombor, and N. Miskolczi, Production of hydrogen rich products from mixture of polyolefin and PET over different modified ZSM-5 catalysts. Chemical Engineering Transactions, 2018. 70: p. 1663-1668.
182. Al-asadi, M., N. Miskolczi, and L. Gombor, Dry reforming of waste polymers in horizontal reactor to syngas production. Chemical Engineering Transactions, 2019. 76: p. 1429-1434.
183. Al-asadi, M. and N. Miskolczi, Hydrogen rich products from waste HDPE/LDPE/PP/PET over Me/Ni-ZSM-5 catalysts combined with dolomite. Journal of the Energy Institute, 2021. 96: p. 251-259.
184. Choudhary, T.V., Kinage, A., Banerjee, S., and Choudhary, V.R., Influence of Si/Ga and Si/Al ratios on propane aromatization over highly active H-GaAlMFI. Catalysis Communications, 2006. 7: p. 166-169.
185. Saad, J.M., Nahil, M.A., Wu, C., and Williams, P.T., Influence of nickel-based catalysts on syngas production from carbon dioxide reforming of waste high density polyethylene. Fuel Processing Technology, 2015. 138: p. 156-163.
186. Erkiaga, A., Lopez, G., Amutio, M., Bilbao, J., and Olazar, M., Syngas from steam gasification of polyethylene in a conical spouted bed reactor. Fuel, 2014. 109: p. 461–469.