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PRODUCTION OF DIESEL FUEL FROM POLYOLEFINS BY PYROLYSIS

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Major in Chemical and Process Engineering

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Abstract of master's thesis

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Abstract

Increasing consumption of plastics has demanded to seek new solutions for the treatment of accumulating waste. Pyrolysis is a chemical recycling method in which plastics are thermally degraded to more valuable products such as chemicals or fuels. The quality of pyrolysis products depends on many factors such as process conditions, reactor type and the quality of feedstock. Plastics are typically originated from the same feedstock as conventional fuels which makes them a desirable choice for pyrolysis treatment. However, they produce a wide spectrum of degradation products and can contain detrimental impurities that produce harmful compounds. With certain process choices and the utilization of catalyst, plastic can be converted to diesel range fuel. Catalyst with low acidity and high porosity is better suited to produce larger molecular compounds. The product can be further processed by various upgrading methods such as distillation, hydrogenation and the use of additives.

The objective of the thesis was to find a route to convert polyolefins to diesel range fuel by pyrolysis. Experimental series was performed with a lab-scale batch reactor in order to seek the most promising catalyst and optimal process conditions. The catalysts tested were ZSM-5, montmorillonite and γ-alumina. The temperature was varied in a range of 500–550 °C. Based on the results, montmorillonite catalyst was chosen to be used in a larger, fluidized-bed unit in temperature range of 475–575 °C. GC/MS, GC/FID and simulated distillation were done to all products.

The results showed that the catalyst shifts the product distribution towards lighter fraction. Average liquid yield was 75 wt.%. ZSM-5 catalyst produced high amount of gases and aromatic components. Montmorillonite and γ-alumina produced mainly liquid in a carbon length range of $<C_{10}$ and C_{11}–C_{21}. Simulated distillation revealed that around 40 wt.% of the product was in a range of $<C_{10}$. In fluidization-bed unit average liquid yield was 70 wt.%. Aliphatic content was 4-5 times higher than aromatic. The proportion of lighter components ($<C_{10}$) accounted 30 wt.% in average. The yield for diesel range fuel increased at lower temperatures based on the simulated distillation. Montmorillonite catalyst yielded promising results and could be a potential candidate for future experiments.

Keywords pyrolysis, polyolefins, thermal degradation, diesel fuel, marine diesel fuel, catalyst, pyrolysis of plastic

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Tiivistelmä

Kiihtyvä muovinkulutus on luonut paineen keksiä uusia ratkaisuja kertyneen jätteen käsittelyyn. Pyrolyysi on kemiallinen kierrätysmenetelmä, jossa muovit voidaan saattaa termisen hajoamisen johdosta pyrolyysinesteeksi, jota voidaan jalostaa kemikaaleiksi ja polttoaineeksi. Pyrolyysinesteen tuotejakauma ja ominaisuudet riippuvat monista seikoista kuten prosessiolosuhteista, reaktorivalinnasta ja raaka-aineen laadusta. Muovit tyypillisesti valmistetaan samasta raaka-aineesta kuin perinteiset polttoaineet, jonka johdosta ne voisivat olla houkutteleva valinta pyrolyysiprosessiin. Muovit kuitenkin muodostavat laajan kirjon eri hajoamistuotteita ja voivat sisältää haitallisia epäpuhtauksia, jotka tuottavat hajotessaan myrkyllisiä yhdisteitä. Muovista voidaan tietyillä prosessivalinnoilla ja oikealla katalyytillä valmistaa polttoainetta, joka voitaisiin käyttää dieselmoottorissa. Etenkin katalyytti, jonka happamuus on alhainen ja huokoisuus suuri, soveltuu paremmin suurimolekyylisten yhdisteiden tuottamiseen. Tämä tuote voidaan jatkojalostaa eri menetelmin, kuten tislauksella, hydrauksella ja lisäaineiden käytöllä.

Tämän työn tavoitteena oli löytää optimaalisin reitti valmistaa dieselpolttoainetta polyolefiineista pyrolyysin avulla. Koesarja tehtiin laboratoriomittakaavan panosreaktorilla, jolla etsittiin lupaavimmat olosuhteet ja katalyytti dieselpolttoaineen tuottamiseen. Testatut katalyytit olivat ZSM-5, montmorilloniitti ja γ-alumiinioksidi. Lämpötilaa varioitiin 500–550 °C välillä. Montmorilloniittikatalyytti valittiin jatkokokeisiin jotka toteutettiin leijupetireaktorilla 475–575 °C lämpötilavälillä. Kaikille tuotteille suoritettiin GC/MS, GC/FID ja simuloitu tislaus analyysit.

Tulokset osoittivat, että katalyytti siirtää tuotejakaumaa kohti kevyempää jaetta. Kokeissa keskimääräinen nestesaanto oli 75 p-%. ZSM-5 katalyytti tuotti suuren määrän kaasuja ja aromaattisia yhdisteitä. Montmorilloniitti ja γ-alumiinioksidi tuottivat pääosin tuotetta hiilijakaumavälillä $<C_{10}$ ja C_{11}–C_{21}. Simuloitu tislaus osoitti, että noin 40 p-% tuotteesta oli alueella $<C_{10}$ p-%. Leijupetireaktorikokeissa keskimääräinen nestesaanto oli 70 p-%. Alifaattisten yhdisteiden pitoisuus oli 1–4 kertaa suurempi kuin aromaattisten. Kevyimpien komponenttien ($<C_{10}$) osuus oli keskimäärin 30 p-%. Dieselpolttoaineen saanto parani alhaisemmissa lämpötiloissa simuloidun tislauksen perusteella. Montmorilloniittikatalyytillä saatiin kokeissa lupaavia tuloksia ja näiden perusteella se voisi toimia hyvänä kandidaattina suuremman mittakaavan koeajoihin.

Avainsanat pyrolyysi, polyolefiinit, terminen hajoaminen, diesel, polttoaine, laivapolttoaine, katalyytti, muovin pyrolyysi

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Abbreviations

PO	Polyolefin
PE	Polyethylene
PP	Polypropylene
HDPE	High-density Polyethylene
LDPE	Low-density Polyethylene
LLDPE	Linear Low-density Polyethylene
ULDPE	Ultra Low-density Polyethylene
VLDPE	Very Low-density Polyethylene
PSW	Plastic Solid Waste
PIB	Polyisobutylene
PB-1	Polybutylene
PS	Polystyrene
PMMA	Polymethyl Metalcrylate
ABS	Acrylonitrile Butadiene Styrene
PVA	Polyvinyl Alcohol
POM	Polyoxymethylene
PET	Polyethylene Terephthalate
PUR	Polyurethane
PF	Phenol resin
PVC	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
MSW	Municipal Solid Waste
BFR	Brominated Fire Retardants
FBR	Fluidized-bed Reactor
CSBR	Spouted-bed Reactor
BFB	Bubbling Fluidized-bed Reactor
CFB	Circulating Fluidized-bed Reactor
CI	Compression Ignition
NCM	Nickel Cobalt Manganese Oxide
MWP	Municipal Waste Plastic
WPO	Waste Plastic Oil
PCDD/F	Polychlorinated Dibenzodioxins/furans
MDO	Marine Diesel Oil
LCA	Life-cycle Assessment
REACH	Registrative, Evaluation, Authorisation and Restriction of Chemicals
ECHA	European Chemical Agency

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Literature Review

1 Introduction

1.1 Background

Due to the population growth, continuous urbanization and social modernization, demand for plastic products in everyday life has gradually climbed for almost past century. Plastic is an essential element in various daily applications which has caused the production rate to reach globally around 300 million tons per year. (1). Recent estimations (2018) suggest that the amount of produced plastic will reach up to 600 million metric tons by 2050. Plastic can be found from almost every daily product from toys and household applications to medical equipment. (2). Polyolefins (PO) which are polymers derived from alkenes contribute most of produced plastics by quantity (3).

The consumption of plastics generates large amount of corresponding waste. In 2018, the waste plastic accounted 29.1 million tons in total post-consumer municipal solid waste in Europe. The bottleneck in plastic waste lies in the recycling and management methods. Of the 29.1 million tons, only 32.5% were recycled, 42.6% were used for energy recovery and 24.6% ended up to landfills (4). Figure 1 illustrates the change in plastic waste management for over ten years in Europe.

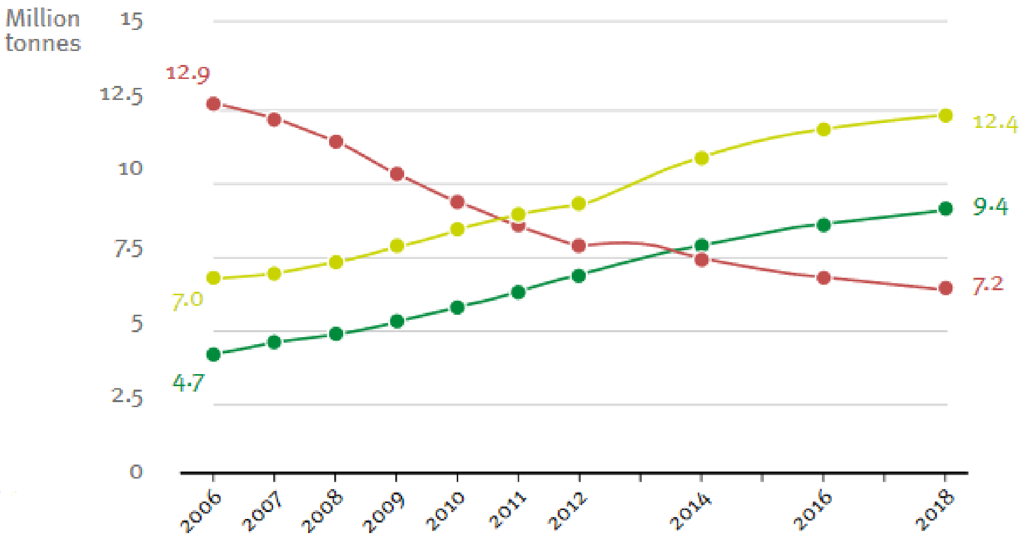


Figure 1. Evolution of plastic post-consumer waste treatment in Europe. Red line represents the landfill, yellow the energy recovery and green recycling (4).

Due to the awareness of society and new legislations, incineration and landfilling are not considered as viable treatment options for plastic waste. Therefore a need towards other treatment options to process the waste has arisen. Many recycling techniques have been developed for plastic waste such as mechanical recycling and chemical recycling. Although mechanical recycling of plastics has increased in recent years, technology is limited by various factors (e.g. efficient sorting). In addition, mechanically recycled plastic tends to possess inferior properties compared to the virgin plastics due to the poor interfacial adhesion. This limits the usability of mechanically recycled plastic in applications. (5).

Chemical recycling, also referred to as feedstock recycling is a method where plastic is converted back to the molecular level. The advantages of chemical recycling compared to the other methods is the high capability to handle all sorts of plastic waste mixtures, whether sorted or unsorted. Chemical recycling techniques include gasification, pyrolysis, liquid-gas hydrogenation, steam or catalytic cracking, viscosity breaking etc. (6).

Pyrolysis is a technique where plastic feedstock is thermally treated in oxygen-free environment which causes depolymerization of long carbon chains. Pyrolysis can be considered as closed-loop recycling if end product is used for similar type of products as virgin material and open-loop if the properties differ from the original material and is used for other applications (7). Product is typically a distribution of solid (char), liquid/wax (pyrolysis oil) and gaseous compounds (8). Product quality and quantity depends on the process conditions and feedstock. For example, low reaction temperature (< 400 °C) favors the production of waxes and heavier oils whereas high temperature (> 700 °C) the formation of gases and lighter oils. (9). Long residence time (also referred to as slow pyrolysis) on the other hand favors the formation of char while shorter residence time volatile products such as oil and gas (10).

Many different applications are researched for the pyrolysis oil and feasible processes already exist for pyrolysis of plastics (11). Pyrolysis products can be utilized in chemical industry, monomer recovery or fuel production (9).

Some petroleum products such as conventional diesel is produced from the same crude oil as plastics. Production of diesel fuel by pyrolysis from plastics could be one solution to reduce the need of crude oil. Plastics are a tempting feedstock to produce hydrocarbon fuels due to the high calorific value and low oxygen content. (12).

1.2 Structure

The objective of the thesis is to conduct a literature review about the pyrolysis of polyolefins, with specific focus on the production of diesel fuel range hydrocarbons. Based on this, experimental work is carried out with different catalysts and process conditions. In literature review, the basic principle of pyrolysis, conditions, properties of the feedstock as well as product quality and comparison of reactor technologies are addressed. Chapter 3 goes in more detail with the production of diesel fuel by pyrolysis. Properties of diesel fuel and quality of feedstock is presented. Process conditions are evaluated in terms of diesel fuel production and the effect on catalyst. Most typical upgrading methods are listed and finally, economical evaluation for the process i.e. energy consumption is discussed.

Experimental part includes the introduction, materials and methods such as short description of the equipment, experimental plan and analysis methods. Finally, results and discussion are presented from the experiments with conclusion and proposal for future work.

2 Pyrolysis of polyolefins

This chapter discusses the pyrolysis of polyolefins in general terms. First, basic principle of pyrolysis is presented, followed by review of polyolefins and related technical problems such as impurities. Process conditions and comparison of reactor technologies are addressed and finally the quality of the product from the polyolefins is presented.

2.1 Principle

Pyrolysis (also referred to as thermolysis) is a chemical recycling method where feedstock is thermally converted back to shorter, less complex units in the absent of oxygen. The chemistry of pyrolysis is complex, and mechanisms are still not fully known. (6). Four cracking mechanisms can be present in the reaction:

- end-chain scission (Equation 1)
- random chain scission (Equation 2)
- chain stripping (Equation 3)
- cross linking (6).

The mechanisms are presented below where M is the monomer.

$$M_n^* \rightarrow M_{n-1}^* + M \qquad (1)$$

$$M_{n-1}^* \rightarrow M_{n-2}^* + M \qquad (2)$$

$$M_n \rightarrow M_x + M_y \qquad (3)$$

Pyrolysis can be practiced with the catalyst (referred to as catalytic pyrolysis) or without (thermal pyrolysis). Products are mixtures of different compounds in gaseous, liquid and solid phases. Typical pyrolysis process includes feeding section, reactor unit, and product collection which has different separation lines, depending on the configuration of the unit. (13). Figure 2 shows a process flow diagram of bench-scale fluidized-bed fast pyrolysis equipment used in VTT technical research centre of Finland.

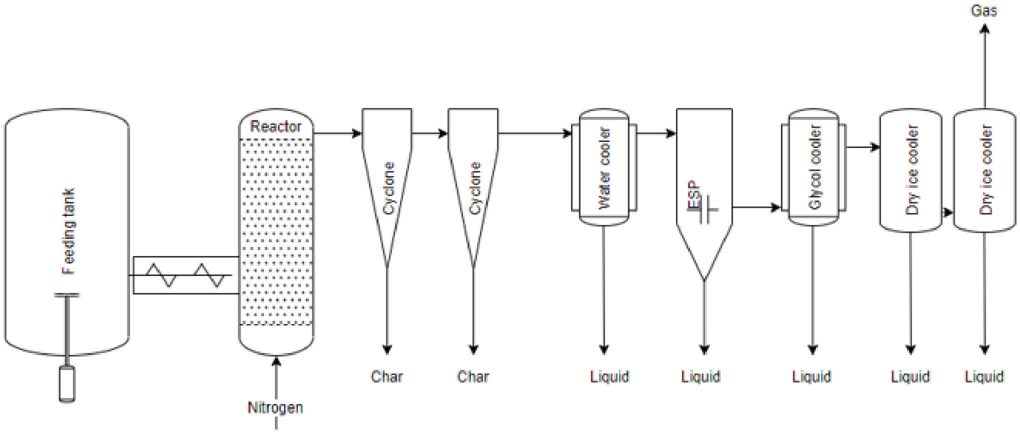


Figure 2. Process flow diagram of bench-scale fluidized-bed pyrolysis equipment.

2.2 Polyolefins

Polyolefins are polymer types produced from olefin monomers, mainly from ethylene and propylene which forms the two most common polyolefins: PE (Polyethylene) and PP (Polypropylene). Several variations of PE are available, based on the density: HDPE (High-density Polyethylene), LDPE (Low-density Polyethylene), LLDPE (Linear Low-density Polyethylene), ULDPE (Ultra Low-density Polyethylene) and VLDPE (Very Low-density Polyethylene). (14). PE is also common plastic in Plastic Solid Waste (PSW), contributing around 40% of total stream. Other notable smaller scale polyolefins are PIB (Polyisobutylene) and PB-1 (Polybutylene). Polystyrene (PS) is not considered as polyolefin but is addressed due to importance in industry. Since the products have similar physical and chemical properties, sorting and separation of the polyolefins is a challenging and cost-effective task. (13).

Polyolefins have similar chemical composition as crude oil, which makes them attractive feedstocks for pyrolysis (13). The properties of polyolefins are listed in Table 1.

Table 1. Properties of polyolefins and polystyrene.

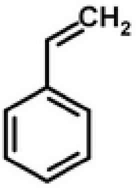
Polyolefin	Structure	Monomer Molar mass [g/mol]	Density [g/ml]	Glass transition temperature [K]	Molar heat capacity [J/(mol K)]	Ref.
PE	$H_2C{=}CH_2$	28.05	0.85–0.90	160–186, 239	59–65	(15)
PP		42.08	0.82–0.90	239–263	88–89	(16)
PS		104.15	1.05–1.06	373–388	125–133	(17)

Table 2 lists some polymers with the evaluation on suitability for the pyrolysis process in terms of liquid fuel production.

Table 2. Products of some plastic types in pyrolysis (18).

Feedstock	Product	Allowance for liquid fuel	Comments
PE	Liquid hydrocarbons	Yes	Thermal pyrolysis usually greater than 500 °C. Can produce wax and lube products (13)
PP	Liquid hydrocarbons	Yes	Higher temperatures are required (13)
PS	Liquid hydrocarbons	Yes	Lower temperatures required (13)
PMMA^1	Liquid hydrocarbons	Yes	
ABS^2	Liquid hydrocarbons	Yes but not suitable	Nitrogen-containing fuel is obtained. Cyanide in oil requires special attention
PVA^3	No hydrocarbons suitable for fuel	Not suitable	Water and alcohol are formed
POM^4	No hydrocarbons suitable for fuel	Not suitable	Formaldehyde is formed
PET^5	Solid products	Not suitable	Terephthalic acid and benzoic acid are formed
PUR^6	Carbonous products	Not suitable	
PF^7	Carbonous products	Not suitable	
PVC^8	Hydrogen chloride and carbonous products	Not allowed	Corrosion occurs
PVDC^9	Hydrogen chloride and carbonous products	Not allowed	Corrosion occurs

1) Polymethyl metacrylate, 2) Acrylonitrile-Butadiene-Styrene, 3) Polyvinyl alcohol, 4) Polyoxymethylene, 5) Polyethylene terephthalate 6) Polyurethane, 7) Phenol resin, 8) Polyvinyl chloride, 9) Polyvinylidene chloride

2.2.1 Impurities

Plastics usually include impurities such as hetero-atoms which reduces the value and can even be detrimental to the pyrolysis process (11).

Major hetero-atoms present in the feedstock are oxygen, nitrogen, chlorine, bromine and fluorine. The elements proceed in the pyrolysis either as intermediate organic compounds in the product oil or as stable inorganic substances such as water, ammonia, hydrogen cyanide, hydrogen chloride, hydrogen bromine, bromine and hydrogen fluoride. (11).

In addition, different sort of metals are present in the waste such as Al, Ca, Na (less than 100 ppm) and Zn, P, Mg, Pb, Fe, Cu, Co, Cr, Ba and Sb (less than 50 ppm). Total ash content (according to analysis) is approximately 0.5–1 wt.%. (19).

Most of the produced plastics include different additives which are used to improve the quality and properties of the product, for example, during shaping of the polymer, extrusion, blow molding etc. In packaging materials, the most used additives are plasticizers, antioxidants, slip compounds, acid scavengers, lubricants, pigments, antistatic agents, flame retardants, light and heat stabilizers and thermal stabilizers. (20).

Plasticizers accounts 10–70 wt.% in plastic products, depending on the type of plastic. Plasticizers enhance the durability, flexibility and stretchability of the polymer. They also plays a role on improving impact resistance. Most typical plasticizers are phthalic esters, dipentyl phthalate, di-(2-ethylhexyl) adipate, di-octyladipate and diethyl phthalates. Antioxidants are used for resistance of overall oxidative degradation of the polymer when exposed to UV light. They usually are added in low amount (0.05–3 wt.%), depending on the chemical structure of the additive and polymer. Most typical antioxidant are arylamines, especially in food packaging. Other antioxidants are phenolics and organophosphates. Heat stabilizers are used to prevent thermal degradation of the polymer in higher temperatures, for example in thermal food processing. They cover 0.5–3 wt.% of the plastic mass and are mainly used in PVC. Typical heat stabilizers are cadmium and lead compounds. (20).

Due to the heterogeneity of the plastic waste, efficient sorting and handling of the feed can be challenging. The separation of polyolefins from other municipal solid waste (MSW) and plastic waste such as polyethylene terephthalate (PET), polystyrene (PS) and polyvinyl chloride (PVC) is easy due to the density differences that allow to use density-based separation techniques. (21). Different automated sorting techniques have been developed to improve the sorting. Brominated fire retardants (BFR) are used in plastics, textiles, electrical and electronic equipment, and furniture to improve fire resistance properties (22). They are one of the most hazardous substances in plastics since the thermal degradation of BFR releases a mixture of different toxic brominated compounds, depending on the feedstock (23).

BFR can be identified with many analysis methods such as by using Near-Infrared (NIR), XRF scanners, Fourier-transform infra-red spectroscopy (FT-IR), high performance liquid chromatography (HPLC), gas chromatography (GC) and mass spectrograph. Density separation is widely used for to separate brominated and non-brominated compounds from each other. As an example, with the addition of magnesium sulphate to the water will increase the solution density to 1.15 g/cm^3, resulting PS plastic waste including bromine compounds sink. However, this technique does not separate different BFR types from each other. (22). Pyrolysis can offer a viable solution to handle plastic mixtures since the process can easily collect pollutants (such as chloride and heavy metals) with modifications of the unit (24). Nevertheless, pyrolysis still cannot necessarily process all types of feedstocks since certain impurities can affect the performance of the catalyst. Carbonaceous residues and hetero-atoms such as Cl and N deactivate the catalyst due to the deposition. If waste stream contains inorganic materials, the reusability can be hindered if compounds are remained with the catalyst which makes pre-treatment steps of feedstock vital. (25).

2.3 Process parameters

In pyrolysis, the product distribution strongly depends on the process conditions. Four main parameters are considered in below: temperature, residence time, pressure and a presence of reactive gases such as steam (13).

2.3.1 Temperature

Temperature plays major role on thermal degradation both in catalytic and thermal pyrolysis. In thermal pyrolysis of polyolefins, operational temperature usually ranges between 350–500 °C. (6). Higher temperatures can be also used (e.g. 700 °C), depending on the feedstock, residence time, aimed products, etc. (26). Overall, the increase of temperature as well as heating rate increases the portion of smaller molecules (11). Higher heating rate increases the rate of reaction and reduces the degradation process time (13). Diesel range hydrocarbon production from plastic wastes ranges between 390–425 °C in thermal cracking (27).

Polyethylene

Polyethylene decomposes at maximal rate in temperature of 420–500 °C. In thermal decomposition of PE, low temperatures yield waxes, paraffins oil and α-olefins whereas high temperatures gas and light oils. (6). At higher temperatures (760 °C), oil/wax portion decrease significantly, yielding more gas products. Studies have revealed that wax formation stops when reaction temperature exceeds 600 °C (13). However, reactor configuration influences this phenomenon, e.g. fixed-bed reactor where feedstock is gradually heated acts contrariwise, yielding high oil ratio at high temperatures. (28). Figure 3 presents an experimental result by Williams et al. (29) where effect on the temperature was experimented with fluidized-bed reactor.

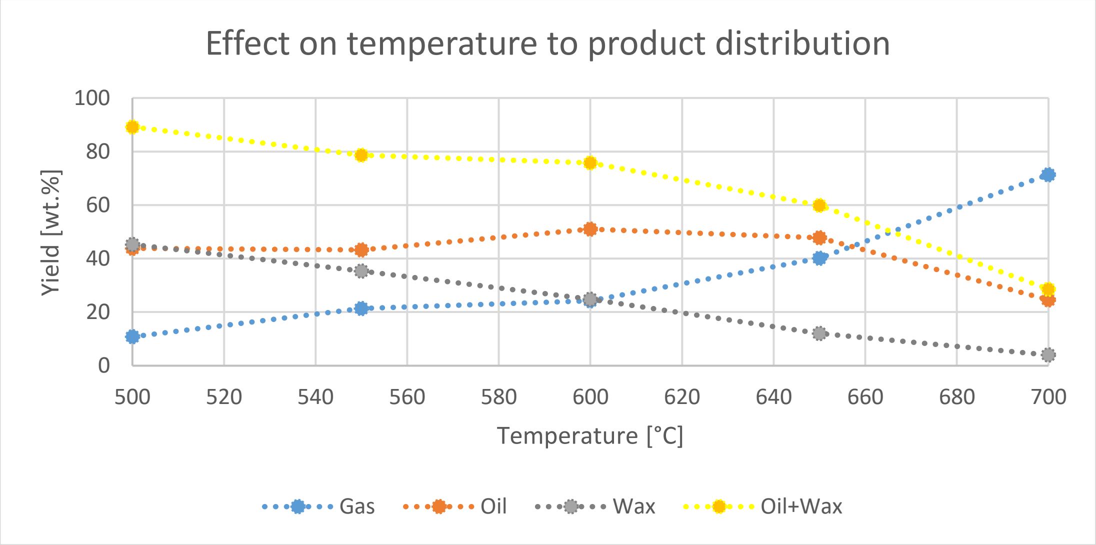


Figure 3. Effect on temperature to product distribution of LDPE feedstock, superficial residence time 15 s. Created from experimental results by Williams et al. (29).

Polypropylene

Polypropylene decomposes at maximal rate in temperature of 400–470 °C (6). Temperature elevation boosts the formation of coke. Additionally, higher temperature increases olefin to paraffin ratio. The peak at condensed hydrocarbons is around at 450 °C. The trend follows that carbon length is shorter at higher temperatures and at lower temperatures the product is dominated by aliphatic hydrocarbons with low amount of aromatics and naphthenes, i.e. wax. (30).

Polystyrene

Polystyrene decomposes approximately in temperature range of 330–425 °C. Main decomposition products are styrene monomers, dimers and trimers. Liquid yield in slow and flash pyrolysis was tested with PS feedstock in temperature range of 400–700 °C. The results showed that liquid yield stays high (>70%) in tested range. Solid formation is highest in slow pyrolysis approximately in 500–600 °C. (24).

Plastic mixtures

Based on the literature, thermal degradation of plastic mixtures occurs at roughly same temperature range than their virgin counterparts (6). At high temperatures, the char and gas yield increases. For example, PE/PS mixture (1:1) produces more gas with lowed liquid yield, compared to the pure plastics. In addition, the trend follows that higher pyrolysis temperature increases the amount of aromatic compounds with the decrease of alkanes and alkenes in product. (24).

2.3.2 Residence time

Residence time is usually based on the chosen pyrolysis temperature. Longer reaction time increases the rate of secondary reactions in the reaction and usually favors the formation of coke, tar and thermally stable products. (11). Short residence time (fast pyrolysis) reduce secondary reactions and increases the formation of wax (31).

Effect on the residence time with HDPE has been studied with a fluidized bed reactor (32). Residence time was varied from 0.64 to 2.5 s in five different temperatures: 650, 685, 730, 780 and 850 °C. Down in Figure 4 is illustrated the relationship between residence time and liquid product yield.

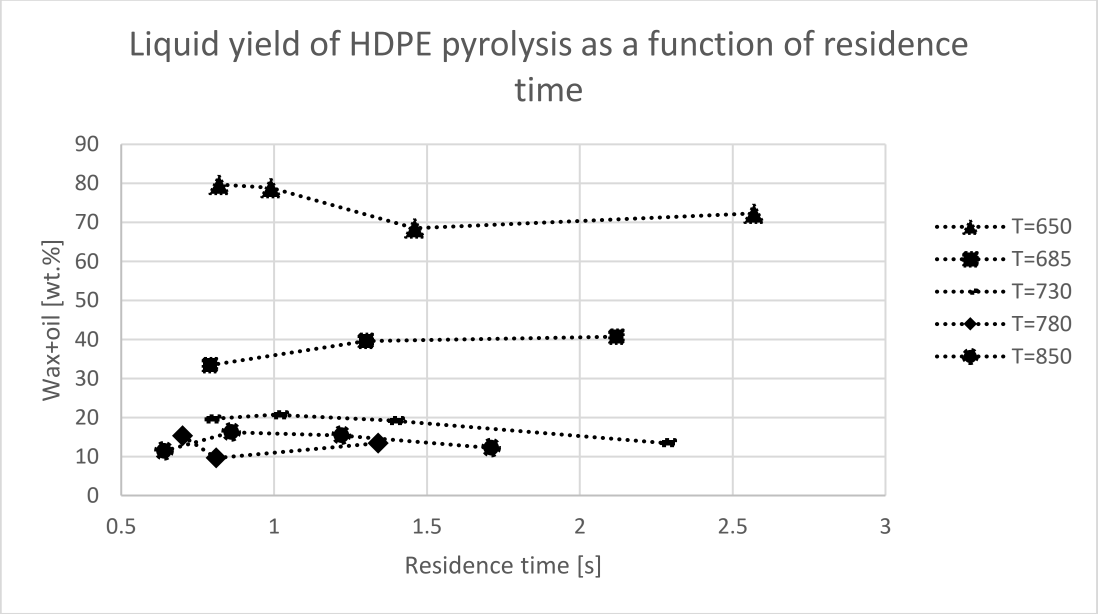


Figure 4. Effect on residence time to product liquid yield with HDPE as a feedstock (32).

Wax formation was most present at 650 °C. At higher temperatures, the wax shifted to liquid-like and the gas yield increased. This was also observed in the study by Mastral et al. where pyrolysis of HDPE was predicted with a modeling tool. When temperature was 650 °C and residence time 0.8 s, wax portion (>C_{33}) was 28 wt.%. The residence time was gradually increased which resulted decrease of wax due to the further cracking of products. (33). Wax formation is especially present with reactor unit that practices fast pyrolysis such as fluidized-bed reactor and conical spouted reactor (34).

2.3.3 Pressure

Pyrolysis is usually performed in atmospheric pressure but there are processes where subatmospheric operations are used. The effect on pressure is not as widely studied compared to the other parameters. Pressure has more significant impact on lower temperatures. Pyrolysis of waste tyres was studied in vacuum process by Lopez et al. in temperature range of 425–500 °C. The effect on vacuum over atmospheric was reported to increase the portion of diesel-range hydrocarbon. (13). This is supported by literature which states that low pressure processes mainly form coke and heavier components (11).

2.3.4 Presence of reactive gases

The presence of additives such as air or hydrogen gas will influence the equilibrium, kinetics and mechanism of the reaction (11). Reactive gases can also be present in certain reactor configuration where gases are circulated back to the reactor as fluidization gas. The presence of air causes oxidation of the feedstock, producing carbon monoxide and carbon dioxide. Steam has been used as an additive gas in the pyrolysis processes. The presence of steam has catalytic effect on the process which shifts the product distribution to gaseous olefins. In addition, hydrogenation causes the elimination of hetero-atoms and enhances the yield towards saturated products. (21, 35).

2.4 Comparison of reactor technologies

The selection of a suitable reactor depends on many process requirements. The most important factors are heat and mass transfer, mixing and residence time. Reactor types can be roughly divided into continuous, semi-batch and batch or combinations of these. (6). For example, continuous reactor types include fluidized-bed reactor (FBR), fixed-bed reactor, spouted-bed reactor (CSBR), extruder, rotary kiln and microwave reactor (13).

2.4.1 Rotary kiln

Rotary kiln is a slow pyrolysis technique in which the feedstock thermally degraded in a circulating tube with external heating. Rotary kilns were mainly used for the production of gases and the processing of plastic wastes (e.g. tyres) (26). Basic principle is presented in Figure 5.

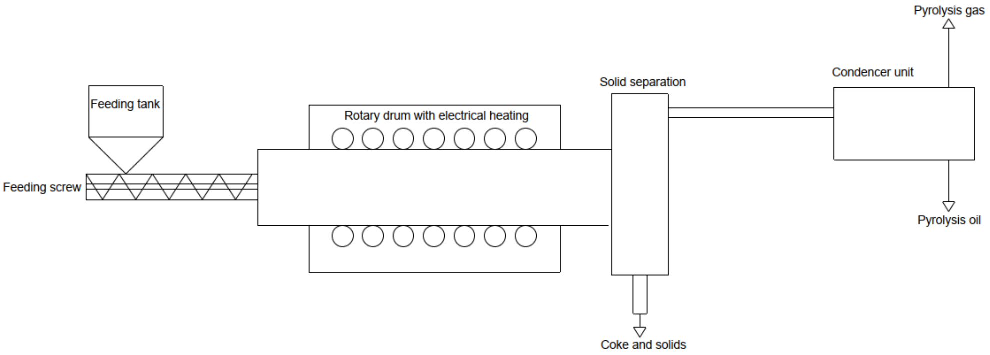


Figure 5. Basic principle of rotary kiln (36).

Rotating kiln is an attractive pyrolysis technology due to its easy operation, flexible raw material, efficient mixing, uniform temperature distribution and low capital cost. In a study by Zhang et. al. pyrolysis of plastics was experimented with a rotating kiln unit. Feedstock was pure plastics (PE, PP, PS) and plastic mixtures. Operational temperature was 500 °C with rotating speed of 6 rpm. Residence time was not stated but it was estimated to be up to 30 min. The results showed that the amount of heat carriers had significant effect on the product distribution. Liquid fraction increased with all feedstocks when the amount of energy carriers was increased. PS gave the best liquid yield. This was theorized to be caused due to the structure of PS, which contains a variety of phenyl groups. (37).

2.4.2 Fluidized-bed reactor

Fluidized-bed reactor is a fast pyrolysis technique where bed of solid particles is kept in fluid-like state with inert gas (e.g. N_2). FBR has many benefits in the pyrolysis such as good heat and mass transfer and easy temperature control. (9). The most important feature of the fluidized-bed reactor is the efficiency and performance of the fluidizing phenomenon. (38). Fluidized-bed reactors have been under research for more than 50 years and many variations have been developed (e.g. bubbling fluidized-bed reactor (BFB), circulating fluidized-bed reactor (CFB) and conical spouted-bed reactor (CSBR) (26). Some benefits and shortcomings of FBR are listed in Table 3.

Table 3. Benefits and shortcomings of FBR (38).

Benefit	Shortcoming
Good mixing of solids	Agglomeration and sintering risk of sticky particles
Uniform temperature profile	Erosion of pipelines and vessels due to the medium
Heat and mass transfer is high	Scale-up challenging
High flexibility	Limited use of different medium*
Lower maintenance costs	Complex design*
	High capital cost and operating costs*

*Especially with CFB

Catalytic FBR process can be done either by *in-situ* where catalyst acts as a fluidized-bed medium and the molten plastic is brought into direct contact with the catalyst or *ex-situ* where the process is two-step with first conventional thermal pyrolysis, followed by a catalytic upgrading product gases (9).

Catalytic pyrolysis of a FBR has proven to be efficient due to good mixing which provides large surface area for the reaction. As mentioned, FBR is a continuous process which makes it suitable for industrial scale since no stopping is required in the process. Plastics can be challenging for the fluidized bed process, as de-fluidization may occur due to molten plastic. This is an important point that needs to be considered in process design. (13).

Residence time in the FBR is short (1–5 s) and small deviation can have big impact on the product distribution. This becomes especially relevant at higher temperatures. (13). Reaction temperature is approximately 650 °C, depending on the feedstock. For example, PE has the maximal yield at T=600 °C and PS at T=500 °C (13).

CSBR is a type of fluidization-bed reactor with a certain reactor geometry. The particles are circulating in uniform way in the reactor, causing efficient mixing and contact with the avoid of agglomeration. (39). CSBR have usually been employed to produce gasoline range products with catalytic process such as with USY zeolite. The benefit of this reactor type is the capability to handle feedstock with large particle size and density. In addition, attrition and bed segregation is not as present in CSBR, compared to other BFB units (13).

2.4.3 Batch/semi-batch reactor

Pyrolysis of plastic has been extensively studied in batch reactors due to their relatively easy design and operation. Batch reactor are usually employed with a stirring device to enhance contact of catalyst and feedstock. (27).

Stirred tank reactor has been used commercially in the production of diesel fuel-like product from plastic wastes. Some examples are Thermofuel™ process and Smuda process. In both processes, continuous stirred tank reactor was used in commercial scale. The operational temperatures were moderately low (350–425 °C) and both utilized reflux operation where heavy components were circulated back to the reactor for further cracking. (27).

Another example of commercial stirred reactor is called NanoFuel® Diesel. The operational temperature was also low (270–370 °C) with a presence of ion-exchange catalyst. The process utilized hot oil as a medium for good thermal conductivity. The process yields 900 l of low-sulfur diesel fuel from 1000 kg of mixed polyolefin feedstock with low amount of non-condensable gases and solid residue. (27).

Batch pyrolysis processes has faced many technical difficulties on larger scale such as residue extraction problems, coking and fouling, corrosion, clogging from waxes etc. and therefore they are not considered viable on an industrial scale (27).

2.5 Properties of pyrolysis oil

The properties of plastic pyrolysis oil strongly depend on the feedstock due to the different degradation mechanisms. For example, polyethylene is degraded by a random chain rupture which produces waxes, paraffin oil and unsaturated olefins. The properties of the oil are also affected by the amount of impurities and heteroatoms in the raw material, especially if plastic waste is used (6).

Plastics contain a wide range of different organic additives (filler, plasticizers, flame retardants etc.). Feedstock containing these sorts of components produce an oil which contains abovementioned substances. In addition, certain components cause instability or low volatility in the oil and produce hazardous compounds in the combustion reaction. (40).

2.5.1 Pyrolysis oil from PE

Pyrolysis oil of PE produces mainly linear paraffins and 1-olefins which are also present in diesel. Linear paraffins tends to form wax which can be problematic in the diesel fuel production. The solubility of n-alkenes is proportional to the temperature which results that at low temperatures crystals begin to form (i.e. cloud point) which is related to the behavior of the fuel. (27). Some upgrading methods for wax are designed that are explained in more detail in Chapter 3.6.2.

2.5.2 Pyrolysis oil from PP

Most of the PP pyrolysis products are olefins and aromatic. Most abundant aromatic in PP oil is propylbenzene (41). Olefins varies from C_5, C_6, C_9, various C_{15} and C_{21} olefins. Among these the most dominating olefins are C_9 olefins, accounting 25% of the total olefins. When PP decomposes, it forms low amounts of coke, but more light components compared to the PE. In study by Kaminsky et al. polypropylene was pyrolyzed with a fluidized-bed reactor at 510 °C (42). It was found that pyrolysis of PP yielded 6.8% gas, 36.7% oils (bp<300 °C), 21.6% light waxes (300 °C<bp>500 °C) and 34.6% heavy waxes (bp>500 °C). Olefins are not desirable products in diesel fuel, ergo refining methods are required for the product to be used in compression ignition (CI) engine. (27).

2.5.3 Pyrolysis oil from PS

PS plays a significant role in the production of plastics and thus in waste stream (around 10% in MSW). Pyrolysis of PS mainly forms styrene monomers. Other products include benzene, ethyl benzene, toluene and trimethyl benzene. PS product has poor flash point and cetane number compared to diesel specifications, thus blending is often required if the product is aimed to use in diesel engine (27). PS has proven in experiments to achieve the best liquid yield compared to other polyolefins (41).

2.5.4 Comparison of polymer products

Table 4 presentes a comparison between the pyrolysis product oils of polyolefins and polystyrene with marine diesel specifications.

Table 4. Comparison of properties between polymer pyrolysis products (27).

Fuel property	**PE**	**PP**	**PS**	**ISO 8217 (DMA)**
Flash point [°C]	33.6	27.8	26.1	min 60
Pour point [°C]	2.7	-39	-67	max -6
Water content [ppm]	0.18	0.13	0.67	–
Ash [wt.%]	0.013	0.01	0.006	max 0.010
Viscosity [mm²/s @50 °C]	2.19	1.9	1.4	max 6 (@40 °C)
Density [kg/m³]	0.858	0.792	0.96	max 1.50
Cetane rating	-	56.8	12.6	min 40
Sulfur [wt.%]	0.01	0.01	0.01	max. 1.5
CV [MJ/kg]	52.3	53.4	50.4	–

As can be seen, the oil properties of each feedstock meet the ISO 8217 marine specifications except with the flash point (27).

3 Production of diesel fuel via catalytic pyrolysis of polyolefins

Diesel fuel is a medium-heavy fuel produced by the distillation of crude oil. However, diesel may include all sorts of selected cracked distillates which are constituents to diesel due to expanding demand. Diesel fuel is intended to be used in CI engines where the ignition is originated from heat of compression, rather than from spark ignition with gasoline fuels. Different definitions for diesel exist, based on the specification used. For example, Europe uses EN590 standard and US ASTM D-975 standard (43). A different standard is used in the marine fuel specification, i.e. ISO 8217 (44).

3.1 Properties of diesel

Diesel consists of hydrocarbons containing principally paraffins, napthenes, olefins and aromatics from which n-alkenes are the dominant components in diesel duel. The content of aromatic compounds in diesel should not exceed 35% by volume as aromatics degrade energy content and reduce cetane number. Olefins are also not desirable products in diesel fuel due to their poor self-ignition capability (45). Carbon range of diesel varies between C_9 to C_{22} (see Figure 6).

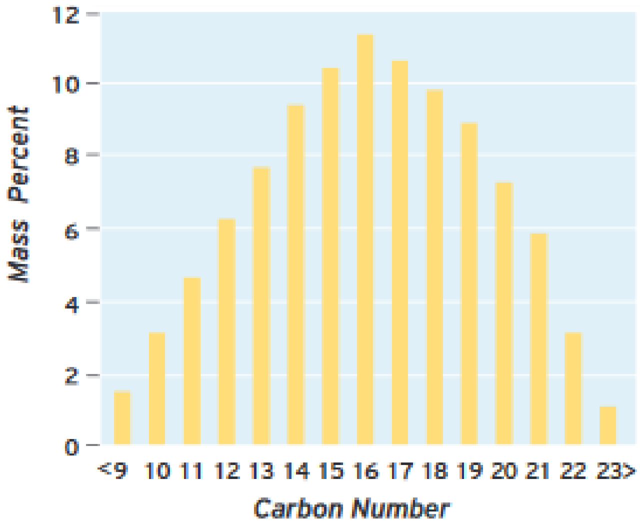


Figure 6. Typical carbon number distribution with diesel fuel (46).

The requirements of diesel properties in Europe are defined in EN590 standard (see Chapter 4.1). (47).

In addition, different specifications for marine diesel oil (MDO) are available which states the necessary properties and boiling point range. As an example, from Neste's selection there are MDO qualities such as RMB, MGO DMA, MDO DMB with boiling point ranges of 180–570, 150–370 and 150–420 °C, respectively (48-50).

3.2 Quality of feedstock

As mentioned in Chapter 2.5, feedstock has significant role on the product quality. The feedstock can include heteroatoms and other excess materials such as metals, glass, cardboard etc. which increases the pre-treatment or post-treatment costs. Typical feedstock input is presented in Table 5 from BP's Grangemouth pyrolysis plant. (27).

Table 5. Typical feedstock composition in BP's Grangemouth pyrolysis plant (27).

Property	Specification	Unit
Polyolefins (LDPE, LLDPE, HDPE, PP)	80	wt.% (min 70%)
Polystyrene (GP-PS, EPS, HIPS)	15	wt.% (max. 30%)
PET	3	wt.% (max. 5%)
PVC	2	wt.% (max. 4%)
Total plastic content	95	wt.% (max. 90%)
Ash	2	wt.% (max. 5%)
Moisture	0.5	wt.% (max. 1%)
Metal pieces	1	max. wt.%
Size	1-20	mm
Fines (sub 250 μm)	1	max. wt.%
Bulk density	400	kg/m³ (min. 300 kg/m³)

In a paper by Dobo et al. transportation fuel production from plastic wastes was studied. The reactor was a batch reactor with reaction temperature of 540 °C. The product was distillated after the experiment (51). The yields for each feedstocks are presented in Table 6.

Table 6. Diesel range yields for different plastic feedstocks (51).

HDPE	LDPE	PP	PS
30.5%	15.2%	24.8%	1.1%

HDPE yielded the highest portion of diesel-range fuel, PP being second. PS gave the highest yield in the gasoline-range among polymers (51).

Pyrolysis of PP and PE feedstock was studied by Khan et al. The aim was to investigate how different feedstock affect the physico-chemical properties of the oil. It was found that properties of PP and PE products were overall same. PP gave slightly lower kinematic viscosity and pour point whereas PE had lower cetane number and diesel index (52). Liquid products were mainly in range C_6–C_{16}, more specifically, the highest portion was found in diesel region, C_{13}–C_{16} (33% and 30% with PP and PE, respectively) (52).

3.3 Process condition

As described in Chapter 2.3.1, thermal degradation of polyolefins is strongly dependent on the temperature. For example, HDPE decomposes at maximal rate in temperature range 420–500 °C.

Process conditions should be relatively moderate to avoid over-cracking. Higher temperatures increase the yield of non-condensable gases and diminishes the portion of heavier components. In fact, it has been stated that with thermal cracking optimum temperature range for diesel product is 390–425 °C. (27, 53).

HDPE and LDPE were pyrolyzed to a diesel-range hydrocarbons in an experiment by Sharma et al. (54). The reactor was a batch type vessel without catalyst. Temperature range was 420–440 °C and reaction time 2 h. Both feedstocks produced mainly paraffins (>90%) with traces of olefins and aromatics. Condensed products were directed to the distillation unit from which the product was separated to four fractions. Two different diesel range fractions were obtained: 190–290 °C and 290–340 °C of which the latter dominated with 41% yield. The carbon length for each feedstock is shown in Figure 7.

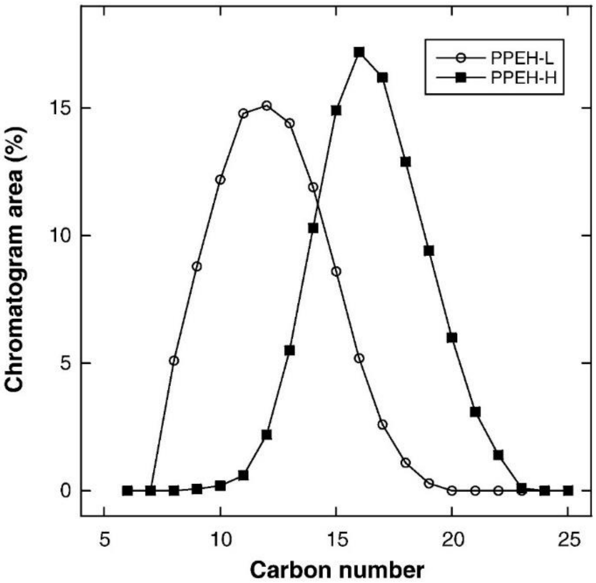


Figure 7. Carbon number distribution between two diesel-range fractions. PPEH-L = diesel range between 190–290 °C, PPEH-H = 290–340 °C (54).

The product properties were measured with AOCS, ASTM and CEN tests with promising results in terms of diesel specifications. Cetane number, sulfur content and moisture met the specification limitations set by EN590 Directive. Cloud point, pour point, oxidative stability and density did not meet the specifications in either fraction. (54).

3.4 Catalyst

The use of catalyst has many practical benefits compared to thermal pyrolysis. With catalytic pyrolysis, operational temperatures are lower and liquid yield better. In addition, catalytic pyrolysis produces a narrower product distribution which has direct impact on oil quality (27, 32). The graph below (Figure 8) shows the effect of the catalyst on the product distribution.

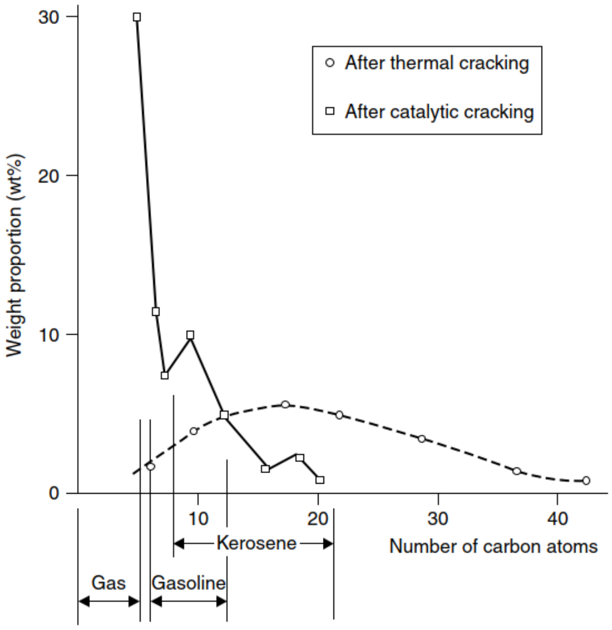


Figure 8. Schematical presentation of yields and carbon length distribution for thermal cracking and catalytic cracking (27).

Catalytic pyrolysis can be performed in either liquid-phase or vapor-phase. In liquid-phase, the catalyst is loaded into the reactor where melted feedstock is contacted with the catalyst and the plastic is converted into the high-value hydrocarbons. The disadvantage of the process is the large amount required catalyst. In addition, the regeneration is usually required so that the operational cost of the catalyst is tolerable. The risk of defluidization can also be present if feedstock is melted on the bed and not thermally degraded efficiently to gas products. In vapor-phase catalytic process, thermal pyrolysis is performed on the first stage, followed by catalytic upgrading. The advantage of this configuration is that unwanted impurities and components can be removed before catalytic reforming section. (25). This set-up is usually performed to produce gasoline range hydrocarbons (27).

Various catalysts have been extensively studied in the pyrolysis of plastics. The most used catalysts in pyrolysis of polyolefins are listed below:

- Acid solids e.g. zeolite, silica-alumina, FCC
- mesostructured catalysts e.g. MCM-41, FSM-16, Al-SBA-15
- aluminum pillared clays
- nanocrystalline zeolites e.g. n-HZSM-5
- superacid solid e.g. ZrO_2/SO_4^{2-}
- gallosilicates
- metals on carbon support
- basic oxides e.g. BaO, K_2O, especially for PS. (39).

The amount, pore size, acidity and contact mode are examples of parameters which affects the behavior of the catalyst and product distribution. The amount of catalyst has been studied in FBR unit to see the behavior of the liquid yield and product distribution. Feedstock/catalyst ratio was tested in range of 1:10 to 1:1. The results showed that overall conversion was not affected by the amount of the catalyst. However, when the amount of catalyst was decreased, the portion of gas and char raised. In semi-batch reactor ratio was tested in range of 200:1 to 4:1. Product distribution showed similar trends regardless the amount of catalyst (39). Reactor design can determine the performance of the catalyst. FBR have superior contact among feedstock and catalyst but in exchange a risk to break and grind the catalyst due to high velocities (27). Literature suggests that acidity of catalyst plays large role on the behavior on the product distribution and quality.

3.4.1 High-acid catalysts

The cracking activity of a catalyst is related to the acidity. Highly acidic catalysts (low SiO2/Al2O3 ratio) tend to have more capability to crack waxes and yield gas products, compared to low acidic catalysts (high SiO2/Al2O3 ratio). (39, 55). Zeolites have been extensively used in catalytic pyrolysis in the production of liquid range hydrocarbons. Many different zeolites are developed for industrial pyrolysis of polyolefins such as ZSM-5, mordenite, X, Y, β, ω. Spent FCC catalyst has also raised interest in plastic catalytic pyrolysis due to the cheap price. (27).

In the study by Akpanudoh et al. the acidity of catalyst was experimented with USY zeolite with PE feedstock. Objective was to study how acidity affects the product yield.

Results indicated that liquid content was maximized with the acidity value of 7%. (56). This corresponded catalyst/feedstock ratio of 4:1.

In a study by Kassargy et al. USY zeolite was used for continuous pilot-scale vertical extruder pyrolysis plant of polyolefins (12). Reaction temperature was 500 °C. The results showed that USY zeolite catalyst provided high amount of liquid (>70% with each feedstock) with carbon distribution of C_1–C_{27}. With PP feedstock, carbon distribution ranged between C_1–C_{15} with 34% of total products between C_5–C_7. PE yielded longer hydrocarbons up to C_{27}. Heavy phase represented around 20 wt.% of the total liquid fraction. (12).

Catalytic pyrolysis was studied with HDPE in four different temperatures (400, 420, 450 °C) and three different catalysts in a batch pyrex reactor. Catalysts were Nickel Cobalt Manganese Oxide (NCM), FCC, HZSM-5. Maximum liquid yield was achieved at T=450 °C, with both thermal and catalytic pyrolysis. The carbon number distribution was broader with T=450 °C (Figure 9) and the yield of diesel-range hydrocarbons were higher. Not clear difference between catalysts was present in the results. (57).

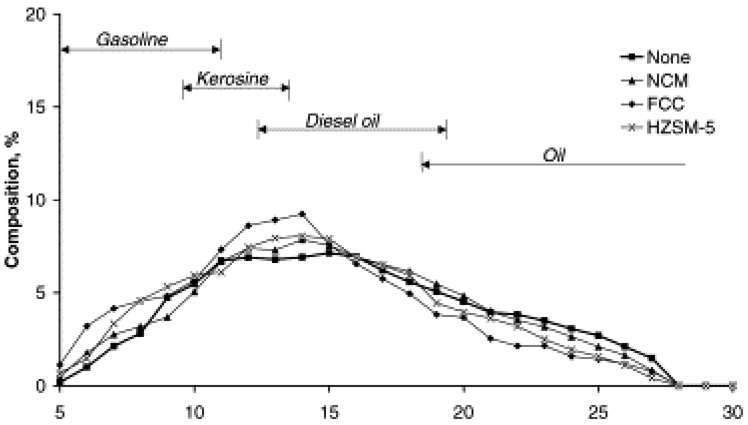


Figure 9. Pyrolysis of HDPE at T=450 °C. Product distribution (57).

Similar results were observed with PS/PE feedstock mixture. It appears that higher temperatures lead to longer hydrocarbon compounds whether catalyst is used or not. The catalyst changes the properties of the liquid by yielding higher aliphatic content and lower aromatic content. Zeolites were compared and concluded that no significant difference was present among FCC, ZSM-5 and clinoptillonite in terms of product yield and composition. The grain size of catalyst was concluded to improve the overall yield due to the higher surface area. (58).

The use of catalyst in many cases favors the formation of lighter hydrocarbons (C_6–C_{12}). In a study by Seo et al. different catalysts were compared with HDPE in reaction temperature of 450 °C in batch reactor (59). Main results are presented in Table 7.

Table 7. Comparison of different catalyst to product distribution (59).

Catalyst	Liquid (%)	Gas (%)	Coke (%)	Liquid fraction distribution (%)		
				C_6–C_{12}	C_{13}–C_{23}	$\geq C_{24}$
No catalyst	84	13	3	57	38	6
ZSM-5	35	64	2	99	<1	0
Zeolite-Y (powder)	2	27	2	97	3	0
Zeolite-Y (pellet)	81	18	2	86	12	2
Mordenite (pellet)	79	19	3	71	29	<1
Silica alumina (powder)	78	21	1	91	9	0
Alumina (powder)	82	16	2	53	43	4

Based on the results, mordenite and alumina are the only catalysts which give high yield (~30 wt.% and 43 wt.%) of diesel-range hydrocarbons besides thermal cracking. The amount of aromatics was highest with ZSM-5 catalyst and the amount of paraffins with alumina catalyst. (59).

The carbon length distribution is related to the pore size of the catalyst. Large pore size leads to longer hydrocarbons. For example, ZSM-5 zeolite provides more lighter components and USY zeolite more heavier components. The shortcoming of large pore size catalyst is more rapid deactivation due to the coke deposition. (27).

High temperature has reported to increase light oil yield with ZSM-5 catalyst. Catalytic pyrolysis of HDPE and PP was studied by Miskolczi et al. ZSM-5 catalyst was used in temperature of 520 °C. The presence of ZSM-5 increased the amount of light oil (C_{12}–C_{28}) with high cetane number (62–69). (60).

One of the problems in zeolites is the sensitivity of the material. Zeolites tends to malfunction and deactivate in the presence of impurities in feed which encourages the use of vapor-phase catalytic upgrading in industrial scale (61).

Vapor phase catalytic upgrading of municipal waste plastic (MWP) was studied in full-scale fixed-bed pyrolysis unit. Thermal cracking was done at 400 °C, followed by catalytic cracking with ZSM-5 catalyst. The product distribution was as follows: oil 80%, gas 15%, residue 5%. Gasoline, kerosene and diesel compositions in the oil were 60, 20 and 20%, respectively. (61).

In many research papers the reactor configuration has been batch or semi-batch unit (54, 56, 57, 59, 62). In these set-ups, the reaction time can be long and heat rate low (5–7 °C/min), compared to other reactor configurations. In short residence time processes such as FBR and CSBR, residence time is short which must be taken into account when comparing the literature results from different authors. In addition, fast pyrolysis processes face different technical limitations and issues than long pyrolysis units.

Catalytic cracking of polyolefins in conical spouted bed reactor was studied by Elordi et al. (63). Catalyst was HZSM-5 zeolite with conditions of 450–570 °C. The results showed good performance on the reactor and slow catalyst deactivation. The portion of heavy liquid fraction (C_{12}–C_{20}) was low (<5 wt.%) in every experiment and not clear trend was visible at different temperatures. In addition, it was clear that with this reactor configuration the temperature should be above 500 °C to avoid technical problems related to the formation of wax. (63).

Two-step cracking has been experimented with conical spouted-bed reactor followed by fixed-bed catalytic reactor where HZSM-5 (SiO_2/Al_2O_3 = 30) zeolite was employed in the second step. Varied conditions were temperature and space-time. (34). Results are presented in Figure 10.

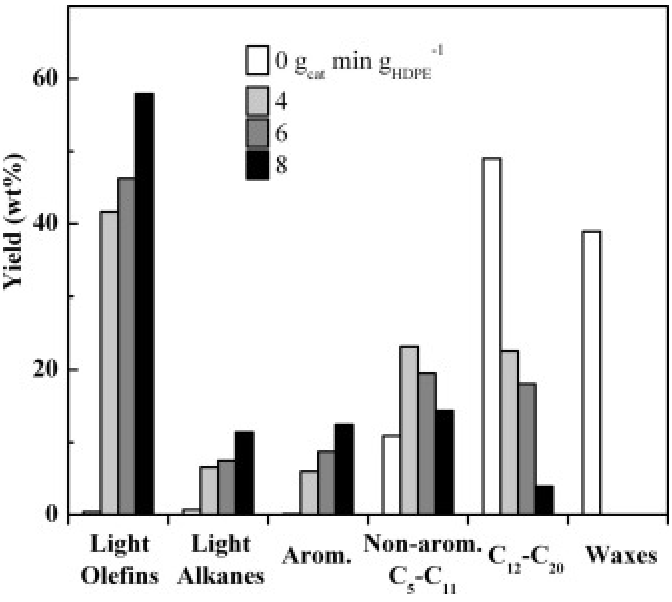


Figure 10. Effect on space-time on product distribution at T=500 °C (34).

As can be seen, space-time has notable effect on the product distribution. Highest portion of heavy-oil fraction was present with space-time value of 0 g_{cat} min $g_{HDPE}{}^{-1}$. Effect on temperature (350–550 °C) was tested with maximum space-time value (8 g_{cat} min $g_{HDPE}{}^{-1}$). The amount of light olefins was high in every temperature but gradually increased in higher temperatures. The amount of non-aromatics was highest at T=350 °C. Yield on the heavy-oil fraction (C_{12}–C_{20}) was low (<10%) on every temperature. In fact, it was reported that the yield of diesel-range hydrocarbons was highest in the absence of catalyst. (34).

3.4.2 Low-acid catalysts

As mentioned, many different non-zeolitic catalysts are studied in pyrolysis of polyolefins such as silica-alumina, MCM-41, $AlCl_3$, natural clay etc. (39).

In contrast to the high acid catalysts which favours the formation of lighter hydrocarbons, less acidic catalysts produce heavier hydrocarbons (27).

Natural clays have been studied in the production of hydrocarbons from plastic feedstock. While the cracking activity can be inferior compared to zeolites, the production of heavier liquid fraction is better due to the lower acidity. Additionally, the deactivation is not as present with clay catalyst than with zeolites. Natural clay catalysts are for example montmorillonite and saponite. (39). The performance of clay catalyst is reported to be influenced by temperature. In a study by Manos et al. clay catalyst was compared with USY zeolite. Below 320 °C, clay catalyst performance was inferior compared to USY zeolite but at higher temperatures the liquid production was 20% higher and provided larger proportion of heavier hydrocarbons. (64). The clay catalysts have also shown promising regeneration ability, resulting practically same level of performance when regenerated via combustion (65).

Pillared and restructured clay catalysts were studied in a paper by Stefanis et al. The comparison between carbon length distribution with non-catalytic pyrolysis and presence of iron/aluminium oxide pillared montmorillonite is presented in Figure 11.

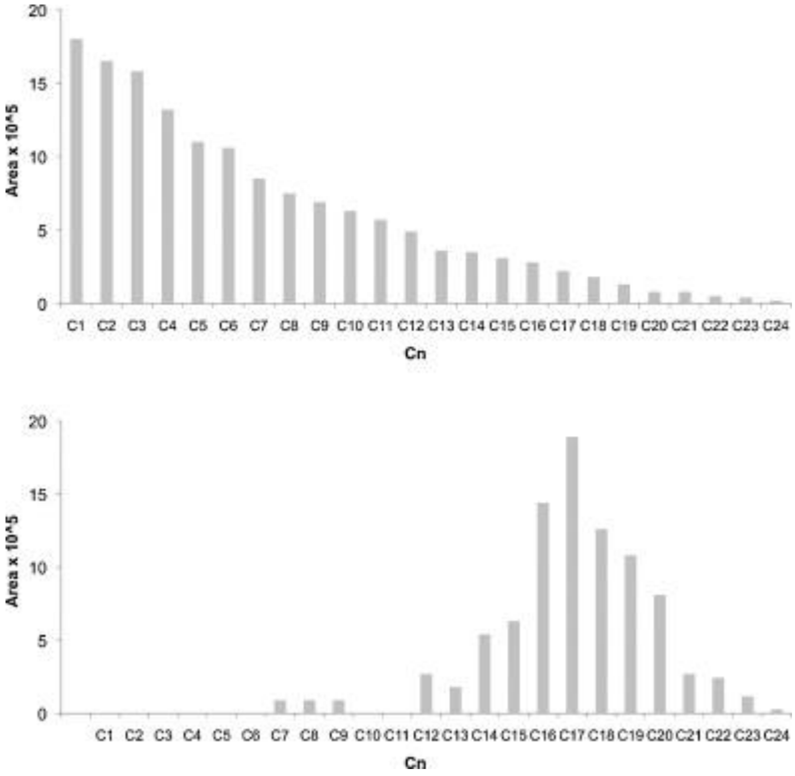


Figure 11. Carbon length distribution in thermal pyrolysis of PE without the catalyst (upper) and presence of clay catalyst (lower). T=300 °C (66).

It shows that the clay catalyst clearly favours heavier hydrocarbons over thermal pyrolysis. High concentration of products ranges between C_{15}–C_{20} (66).

The clay catalyst produced large amount of aliphatic hydrocarbons and a small amount of aromatics whereas H-ZSM5 mainly produced gases and aromatics (66).

Sakata et al. studied thermal degradation of PE and PP with solid acid catalyst and non-acid catalyst. Acid catalysts were silica-alumina (SA-1, SA-2), ZSM-5 and non-acid silicalite, mesoporous silica gel and mesoporous folded silica (FSM). Of these catalysts, the low-acid catalyst, i.e. FSM produced the best yield for heavier hydrocarbons and least amount of gases. (67).

In conclusion, it would be recommended in production of diesel range fuel that the catalyst have low acidity and large pore size. A summary of catalytic pyrolysis experiments with various reactor configurations is presented in Appendix 1.

3.5 Performance in CI engines

The performance of catalytic waste plastic oil (WPO) from plastic mixtures in diesel engines has been studied by Mani et al. with promising results. Test shows that the diesel engine can utilize a variety of blends and pure plastic pyrolysis oil. Main observations are listed below:

- NOx emissions are generally higher by 25% with PO
- CO emissions are 5% less with PO
- Unburned hydrocarbon emissions are 15% higher and thermal efficiency is up to 75% of the rated power (68, 69).

Other engine performance factors such as brake thermal efficiency (BTE), brake specific fuel consumption (BSFC) and brake power (BP) are also tested. Table 8 shows the comparison between plastic waste oil and conventional diesel.

Table 8. Results from engine testing of WPO and diesel oil (69, 70).

Item	Diesel	WPO	Blend 20:80 WPO:diesel
BTE [%]	25.1	27.4	25.9
BSFC [kg/kWh][1]	0.7	-	0.6
BP [kW][1]	0.7	-	0.6
CO emissions [%]	0.8	-	0.08
HC emissions [ppm]	19	-	24

1) At 25% load

The information on the pyrolysis process such as reactor type, catalyst, conditions etc. were unavailable. The catalytic pilot pyrolysis process uses various feedstocks such as PE, PP, Teflon, Nylon and Dacron (69).

Same pyrolysis oil has been tested to blend with marine fuel. Tests showed that with the mixture of pyrolysis oil and marine heavy fuel can reduce NOx emission significantly and affect the viscosity of the fuel. (68).

3.6 Upgrading methods of pyrolysis product

Plastic pyrolysis product is generally unsuitable for diesel engine due to unsaturated compounds, impurities, and wide range of different hydrocarbons. Many upgrading methods have been developed to enable diesel fuel to meet the set directives. Upgrading methods used in industry are for example hydrogenation, distillation, use of additives and catalytic upgrading.

3.6.1 Hydrogenation

Hydrotreating is generally employed to the pyrolysis fuel to convert unsaturated olefinic end groups to saturated groups and to remove sulfur from the stream. In addition, hydrogenation increases oxidative stability and improves thermal stability as well as affects to the color of the product. (27).

Hydrogenation was studied as an upgrading method for pyrolysis oil by Horvat et. al with PE (53). In the experiment, temperature and residence time were varied in semi-batch reactor to find best variables for hydrogenation treatment. Temperature was varied between 400–440 °C and nitrogen flow rate was adjusted so that superficial residence time ranged between 1–14 min. The main interest was the proportion of n-alkenes, 1-alkenes, and linear products since they have important role on determining the quality of the product to be used in hydrogenation. Results showed that the effect on the temperature and residence within the tested range had no significant effect on the proportion of these compounds. Hydrogenation was performed in stirred batch autoclave at 70 °C and 41 bar with United Catalysts T-2464. The product shifted from yellowish to clear with 110% of increase in n-alkene conversion. While the product quality was greatly enhanced with hydrogenation process, refinement was still required for the oil to meet standard specifications. (53). Hydrogenation of PP pyrolysis product was also studied with catalyzed pyrolysis product. Hydrogenation was performed with Ni/ZSM-5 catalyst. Pyrolysis product had paraffins, olefins and naphtenic hydrocarbons portion of 66.6%, 25.7% and 7.6%, respectively. After the hydrogenation unit, the portion of olefins was diminished to practically zero, with 97% of alkanes and some aromatics. In addition, flash point and kinematic viscosity met the EN590 requirement after the upgrading. Carbon range also was much closer to diesel range after hydrogenation. (71).

3.6.2 Catalytic dewaxing/isomerization dewaxing

Catalytic dewaxing is used to crack longer chain n-paraffins into more suitable compounds for diesel fuel. Usually aluminosilicate zeolites (e.g. ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38) are used for catalytic dewaxing due to the nature to crack n-paraffins but exclude other more branched compounds. The upgrading technique is usually performed in PE based product which produces waxes from pyrolysis. (27).

Catalytic isomerization dewaxing is used to isomerize n-paraffins into iso-paraffins, which lowers the cloud point, pour point and boiling point range but keeping high cetane number. Typical catalysts are ZSM-22 and ZSM-23 due to the large pore size. (27).

An institute named Clariant and Duslo’s research institute VUCHT utilizes specially designed HYDEX E catalyst for hydro-dewaxing of polyolefin products. The process is a pilot-scale unit which converts the feedstock into winter-grade diesel oil. (72).

Thermal cracking of polyolefins tends to form waxes (up to 65%) with low residence time (FBR, CSBR) which makes dewaxing tempting operation as upgrading operation (34).

3.6.3 Distillation

For pyrolysis product to be suitable for diesel engine, the properties (e.g. viscosity, ash content, cloud point) must fulfill the technical specifications. Distillation is one of the proposed methods to upgrade the pyrolysis product into diesel-like fuel. (18). The product is fed to the distillation column where fractionation occurs based on the distillation temperatures of the liquid. Important parameters in distillation are reflux ratio, temperature of reboiler, temperature gradient and pressure. (25). Illustrative diagram of distillation unit is presented in Figure 12.

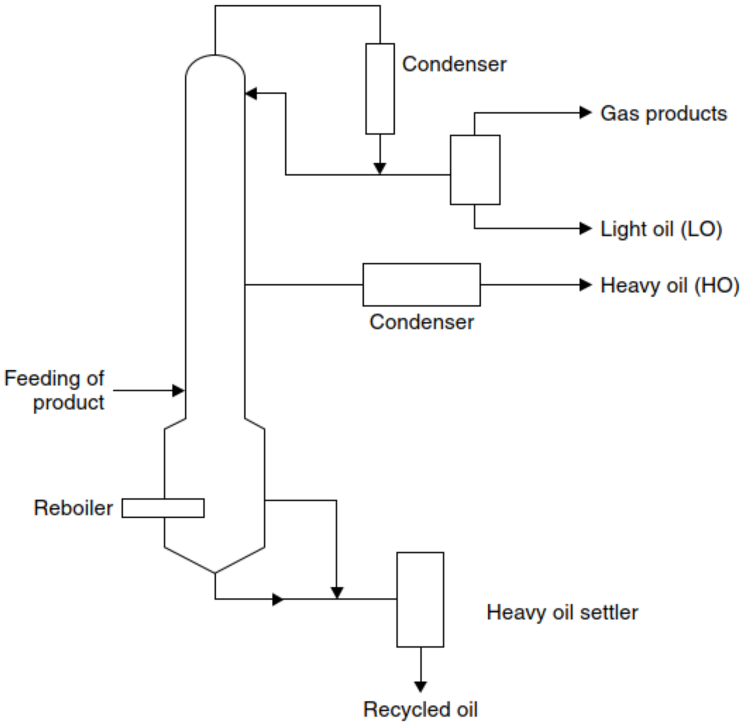


Figure 12. Illustrative diagram of distillation unit of pyrolysis product (25).

In the study by Kassardy et al. described in Chapter 3.4.1, pyrolysis product was distilled after catalytic degradation. Optimal distillation temperature for heavy fraction of the oil was found at 220 °C. The properties of the product were compared with the diesel fuel standard EN590. It was found that with PE feedstock, cetane number, viscosity and flash point met the requirements set by standard EN590. With PP and 50-50 mixture PE/PP viscosity and flash point were within the spec yet cetane number was slightly less (42.2 and 45.1, respectively) than minimum required. (46). The cetane number can be overcome by the fact that according to the Directive

2009/30/EC diesel fuel must be blended with 7% of biodiesel. This was tested in the same experiment which increased the cetane number up to 52.5. (12).

3.6.4 Centrifuge

If feedstock involves water, centrifuge is a typical installation to the process to remove water content from the product. Centrifuges can separate water, diesel and sludge, providing higher value end-product. In case of high carbon residue content on the fuel, ultracentrifuge can be introduced for the process. (27).

3.6.5 Additives

In diesel fuel, additives are usually added to the product to enhance different properties for it to meet set specifications. Two important parameters are cloud point and pour point. Cloud point determines the temperature where crystals start to form, causing cloud or haze appearance. Pour point is the temperature where the product takes gel-like state and loses the flow characteristics. Different additives are used to enhance the abovementioned properties. For example, cloud point can be reduced by adding styrene monomers since paraffinic compounds are more soluble to styrene than diesel. In addition, by adding mixing oil to the product has positive impact on the cloud point. Trademarked additives (e.g. Callington Haven Roxdiesel Pour Point Depressant) are developed to reduce the pour point of diesel. (27).

3.7 Economical and environmental evaluation

Pyrolysis is an energy intensive process due to the high process temperatures and different steps from handling of the feedstock to recovery of product. Table 9 shows an example of main economical aspects from pilot-scale pyrolysis process.

Table 9. Economical aspects from pyrolysis process (60).

Item	Value	Unit
Raw material handling	65–285	€/t
Collection	20–100	€/t
Classification	10–50	€/t
Washing and shredding	10–90	€/t
Transportation	25–45	€/t
Electric energy	200–300	kWh/t raw material
Heating gas	200–350	m³/t
Cooling water	90–150	m³/t

An exact evaluation is hard to make which can be seen from the deviation of the values. Especially with raw material handling, even larger values have been reported. Values heavily depends on the process and process configurations used (60).

Important economical value is the cost of catalyst. If the catalyst cannot be recovered/reused or it has very short lifespan, the catalyst price can take significant portion of operational costs (73).

Economical efficiency also depends on the process unit. For example, FBR has flexibility to operate larger scales with high capacity which brings the operational costs lower, compared to smaller unit (19). Decentralization has its own benefits such as small distances to deliver solid feedstock. On the other hand, if integrated unit is used at the refinery, any formed product gases could also be utilized to the process. In addition, feedstock availability needs to be addressed before setting up a plant. Some benefits and drawbacks are compared in Table 10.

Table 10. Comparison between small scale and large scale units (19).

Item	Small scale unit	Large scale unit
Investment costs	🟩	🟥
Exploitation costs	🟥	🟩
Co-operation with refinery	🟥	🟩
Feedstock deliveries	🟩	🟥
Diversification	🟩	🟥

3.7.1 Energy consumption

When considering the energy consumption of pyrolysis, three main energy requirements are needed to consider: evaporation of moisture, supply of melting and latent heat and supplying the heat of reaction from feedstock.

One viable process design when considering energy consumption is energy integration. For example, the heat of condensation of product vapours can be utilized in many process steps such as preheating of the feed which reduces the heat requirement for the process or by using the heat in refinery steps such as distillation (11). The distillation step also fractionates light vapours (Figure 12) that can be directed back to the pyrolysis unit as a fuel (25).

For the process to be sustainable and environmentally viable, the energy consumption must originate from renewable sources. Pyrolysis reactor is usually powered with electricity to keep wanted temperature. Already existing publications regarding the use of different renewable sources of electricity are available, for example, solar assisted pyrolysis. (74, 75).

Some of the benefits of using solar assisted pyrolysis is listed below

- Economically viable option, 86$/MWh
- Low greenhouse gas emissions, 162 kg CO_2/MWh
- Reduced fuel costs, by one-third

Grid-tied solar photovoltaic/shrouded wind turbine solar system was employed in pyrolysis reactor in a study by Ghenai et al. to produce diesel-range hydrocarbons (76). The results showed that all energy demands were met with this power unit. Simulation was performed with off-grid and grid-tied configurations. The former showed better performance on the CO_2 emissions and renewable fraction but with higher electricity costs (180 $/MWh) and the latter more sustainable choice with lower electricity cost (70 $/MWh) and low CO_2 emissions (44.1 kg CO_2/year). (76).

3.7.2 Environmental impact

Pyrolysis offers better environmental advantages, compared to other waste management options. Due to the absence of oxygen in the process, pyrolysis does not form any harmful dioxins in the reaction. Pyrolysis process reduces carbon footprint with reduced CO and CO_2 emissions (13). All the products are collected in pyrolysis process and utilized (77). MSW contains a lot of different contaminants such as K, P, S, Br, Sb, Cl, Ca, Fe, Zn and Cr atoms. Pyrolysis process can exclude efficiently these contaminants, resulting cleaner product. Important note is the presence of polychlorinated dibenzodioxins/furans (PCDD/F) in the MSW. In pyrolysis study, it was clear that these sorts of compounds end up to the product even though pyrolysis process has detoxificate effect. (77). The amount of PCDD/F can be reduced with hydrothermal treatment. In a paper by Chen et al. Cl removal and PCDD/F detoxification were studied with hydrothermal treatment method. The results showed combination of hydrothermal treatment and pyrolysis reduced the amount of these compounds by 90%. (78).

Environmental impact of pyrolysis process has been assessed in some studies (79-81). The environmental impact for pyrolysis depends on the system boundaries and limits. For example, boundaries such as location, interactions with neighbouring systems, time and date, including the capital costs and technology used are important to state when doing life-cycle assessment (LCA) (81). Pyrolysis has significantly lower environmental impact compared to the incineration. The environmental effect is related to the end-product. For example, it was reported that if the product is wax, lowest climate change was achieved. If light oil was produced, smallest fossil depletion was achieved and with heavy oil, lowest acidification (80).

3.8 Challenges

3.8.1 Catalyst limitations

In catalytic pyrolysis, one of the challenges is the formation of coke. The coke forms deposits in the reactor and causes the catalyst to deactivate. Also, the use of catalyst increases the running costs, especially if catalyst becomes easily poisoned or otherwise requires disposal. Coke formation is more present in catalysts with large pore size since coke deposits can form more easily inside the pores. (27).

As mentioned, zeolite catalysts are rather sensitive towards impurities in the feedstock. For example, the presence of HCl, originated from PVC feedstock ruins the catalyst when the concentration exceeds above 200 ppm (27).

3.8.2 Instability of fuel

One of the most important properties of a fuel is the stability. The product may begin to deteriorate soon after manufacturing due to repolymerization and oxidation. This is due to the presence of unsaturated fuel molecules linking together in the fuel. The components begin to form sediment and insoluble compounds that sink to the bottom of the container, forming sludge. Stability can be affected by the addition of additives to the diesel that prevent polymerization and oxidation. The additives are usually employed at the cracking process, in the run-down section when the product is hot and recently produced. Commonly used additives is Octel FOA-6. (27).

4 Standards and specifications

One of the challenges on commercializing pyrolysis oil is that the product has no standardization which could be used in marketing. A proper definement is required to normalize the product and to utilize it in applications. In this section, EN590 standard for European diesel fuel is presented as well as ISO 8217 for marine diesel fuel. In addition, REACH regulation is discussed in respect to pyrolysis fuel product.

4.1 EN590 Standard

EN590 standards for diesel fuel is presented in Appendix 2.

4.2 ISO 8217 Standard

ISO 8217 standard is used to specify the petroleum fuel requirements for marine diesel engines and boilers. ISO 8217 standard is presented in Appendix 3.

4.3 REACH

Registrative, Evaluation, Authorisation and Restriction of Chemicals (REACH) is an EU regulation set up in 2007 with aim to ensure safe manufactory and use for all produced substances. All chemical producers with capacity over one tonne per year must register the chemical to European Chemical Agency (ECHA) in order to the product to be marketed in EU market. A hazard and potential risk must be assessed to the chemical for producing and importing. If the substance is a carcinogenic, toxic for reproduction or mutagenic (CMR), polybutylene terephthalate (PBT) or very persistent and very bioaccumulative (vPvB), it may be identified as Substance of Very High Concern (SVHC). This can also be proposed by Member State of ECHA. The authorization can be applied in two-step process where the substance is first listed as SVHC to become a part of Candidate list by ECHA. After two-step regulatory process, it may be included to the Authorisation list and can be manufactured in EU area. Incidentally, polymers are not addressed in REACH due to the high molecular weight and falls to cray area in REACH definition. For example, impurities (e.g. stones, plastics, rubber, sand, paint, coating etc.) used in the plastic are considered as part of the substance if it does not exceed total of 20% by weight and are not recycled in purpose in the process. In REACH, there is no clear line between which is considered as impurity. ECHA guideline states that impurity is “an unintended constituent present in a substance as produced. It may originate from the starting materials or be the result of secondary or incomplete reactions during the production process. While it is present in the final substance it was not intentionally added.” This means that any impurities which were included in the polymer at the beginning, must be in the final product, to comply with REACH. (22).

5 Summary

Plastics are potential feedstocks in fuel production due to the high energy content. Most abundant plastic types are polyolefins which are produced from straight alkene monomers. Plastics include many different excess materials and impurities which can be detrimental to process or catalyst and must be removed. Pyrolysis is a chemical recycling technique which converts plastic into more valuable components via thermal treatment in oxygen-free environment. Pyrolysis process is affected by many parameters such as process conditions, reactor type, the presence of catalyst and feedstock type. Many authors have studied the suitability of plastic waste into diesel fuel engine. The key issue is to meet set standards for diesel engine. In addition, pyrolysis product usually include olefins which are not suitable for CI engine due to the poor ignition properties. The choice of catalyst plays a major role in the product distribution. Catalysts with low acidity and large pore size have demonstrated to give better yield to heavier liquid components. The liquid is rarely suitable to be used in the engine and therefore various upgrading methods exist to enhance pyrolysis product such as distillation, hydrogenation, dewaxing and use of additives. Pyrolysis process is energy intensive process which requires continuous energy input due to the endothermic behavior. One of the solutions to tackle with this problem could be to practice energy integration in the process, e.g. circulating the process gases. The energy for the process should also originate from renewable sources. Pyrolysis has proven to efficiently collect hazardous substances such as BFR and reduce the carbon footprint. Plastic pyrolysis oil per se does not have any standardization which could be used as a guideline to normalize the product which is one area for development. Pyrolysis liquid from plastics is not specified in REACH. Plastic recyclers must comply with set obligations to commercially sell the product in Europe, but the guidelines are subject to interpretation in terms of plastic waste and more clarification is required in the field.

Experimental part

6 Introduction

The objective of the experimental work was to screen different catalysts and find the most optimal parameters to produce diesel-range product. Materials and methods used in this experimental study are introduced in Chapter 7. Raw material, catalyst, description of the units, operational constraints and analysis methods are addressed. The results and discussion of the experiments are presented in Chapter 8. The work is concluded in Chapter 9.

Experimental plan is presented in Table 11. The screening experiments were performed to test different catalysts and conditions. Total of three different catalyst were tested at three temperature points. The amount of feedstock, carrier gas and catalyst/feedstock ratio were fixed. Plan included one repeated experiment (run #13). Bench-scale fluidization-bed experiments were carried out where the most promising catalyst was chosen for larger unit. Varied parameter in the abovementioned unit was temperature. Residence time was chosen to be kept fixed throughout the experiments.

Table 11. Experimental plan

<table>
<tr><th colspan="3">Batch reactor experiments</th></tr>
<tr><th>Run #</th><th>T [°C]</th><th>Catalyst type</th></tr>
<tr><td>1</td><td>500</td><td>No catalyst</td></tr>
<tr><td>2</td><td>525</td><td>No catalyst</td></tr>
<tr><td>3</td><td>550</td><td>No catalyst</td></tr>
<tr><td>4</td><td>500</td><td>ZSM-5</td></tr>
<tr><td>5</td><td>525</td><td>ZSM-5</td></tr>
<tr><td>6</td><td>550</td><td>ZSM-5</td></tr>
<tr><td>7</td><td>500</td><td>Montmorillonite</td></tr>
<tr><td>8</td><td>525</td><td>Montmorillonite</td></tr>
<tr><td>9</td><td>550</td><td>Montmorillonite</td></tr>
<tr><td>10</td><td>500</td><td>γ-alumina</td></tr>
<tr><td>11</td><td>525</td><td>γ-alumina</td></tr>
<tr><td>12</td><td>550</td><td>γ-alumina</td></tr>
<tr><td>13</td><td>550</td><td>γ-alumina</td></tr>
<tr><th colspan="3">Bench-scale experiments</th></tr>
<tr><th>Run #</th><th colspan="2">T [°C]</th></tr>
<tr><td>14</td><td colspan="2">475</td></tr>
<tr><td>15</td><td colspan="2">500</td></tr>
<tr><td>16</td><td colspan="2">525</td></tr>
<tr><td>17</td><td colspan="2">550</td></tr>
<tr><td>18</td><td colspan="2">575</td></tr>
</table>

7 Materials and methods

Materials and methods are presented below. The section includes feedstock composition, catalyst, description of the unit, parameters and analysis methods.

7.1 Raw materials

The feedstock composition is presented in Table 12. Polymers used in the experiments were LDPE, HDPE, PP and PS which is based on the literature review of the typical composition of plastic waste (82). Any other substances such as other polymers and impurities are excluded in this work. Same feedstock was used in all the experiments.

Table 12. Feedstock composition

Polymer type	Portion [wt.%]	Origin
LDPE	35	Exxonmobil chemical
HDPE	29	Exxonmobil chemical
PP	22	Total Polymers
PS	14	N/A

7.2 Catalyst

Properties of the catalysts are described in Table 13. Information on the pore volume of ZSM-5 catalyst was unavailable.

Table 13. Properties of the catalysts.

Property	ZSM-5	Montmorillonite	γ-alumina
Density [g/cm³]	>1	0.37	0.83
Surface area [m²/g]	400	240	225
Pore volume [cm³/g]	N/A	0.26–0.36	0.59
SiO_2/Al_2O_3	280	5.12	-
Product name	CBV 28014 (Zeolyst)	Montmorillonite clay extruders (BDH Chemicals Limited)	Harshaw Chemical Co.

Catalyst/feedstock ratio was set to be 1:1 in batch experiments, based on the literature (Chapter 3.4). The catalyst was located into bottom layer of the reactor and sand medium (Al_2O_3) on top which allowed the feedstock to thermally decompose before being in contact with the catalyst bed. In fluidization-bed reactor experiments, the amount of catalyst was chosen to correspond the volume of typically used bed medium. This was done to ensure steady and homogeneous heat profile inside the reactor. Calculated weight hour space velocity (WHSV) was 1.73. Figure 13 illustrates the catalyst contact mode in both configurations.

Batch reactor (BR)	**Fluidized-bed reactor (KILO)**

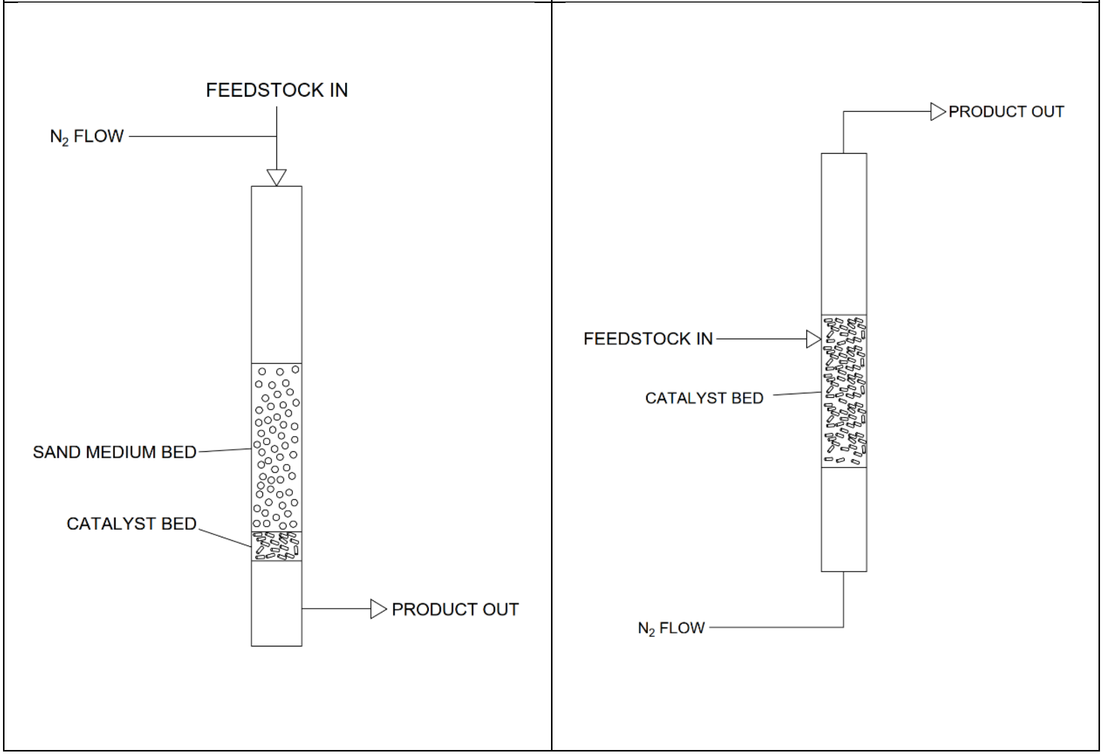


Figure 13. The illustration of catalyst contact mode in both reactor configurations.

In fluidized-bed reactor experiments, the chosen catalyst needed to be tested to find minimum fluidization velocity. Cold fluidization test was performed in a plastic tube with attached pressure indicators and mass flow meters (Figure 14). The catalyst was first tested in a state as ordered, but it was soon discovered that sorting of the particles was present during the fluidization. To achieve better catalyst behaviour in the reactor, sieving of the catalyst to narrower particle size was carried out. Catalyst was sieved to the same particle size as used bed medium in fluidized-bed unit (i.e. 0.56–0.71 mm). Results from fluidization test is presented in Appendix 4.

Figure 14. Cold fluidization tests with used catalyst.

Minimum fluidization velocity for the catalyst was 0.2 m/s which corresponded 25 l/min. Charles's law was used (Equation 4) to calculate the volumetric flow in operational conditions.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \rightarrow V_1 = \frac{V_2}{T_2} T_1 = \frac{25\ l/min}{(273+500)K} * 273\ K \approx 9 \frac{l}{min} \qquad (4)$$

Therefore, fluidization velocity for operational temperature of 500 °C was set to 9 l/min in the reactor in order to reach minimum fluidization velocity.

In the BR experiments, the catalyst was regenerated by burning the catalyst after each experiment. The burning was done at temperature >600 °C for 1-2 hours to ensure sufficient regeneration. In KILO experiments the catalyst was replaced after each experiment.

7.3 Description of the unit

The description of batch reactor and fluidized-bed reactor are introduced respectively below.

7.3.1 Batch reactor (BR)

Catalytic pyrolysis screening experiments were performed with a lab-scale batch reactor (BR) (Figure 15). The unit is a tube type reactor with diameter of 5.4 cm and height of 21.9 cm, it includes external heating oven, two inlets for nitrogen and oxygen as well as collection section for products. Collection section consists of three glass bottles in an ice-water bath. Exit gas is directed to a gas bag for later analysis. Temperatures are controlled from a control panel. The feedstock is dropped from the top section of the unit with two valves which allows inertisation of the feed.

P&ID of the unit is presented in Figure 16.

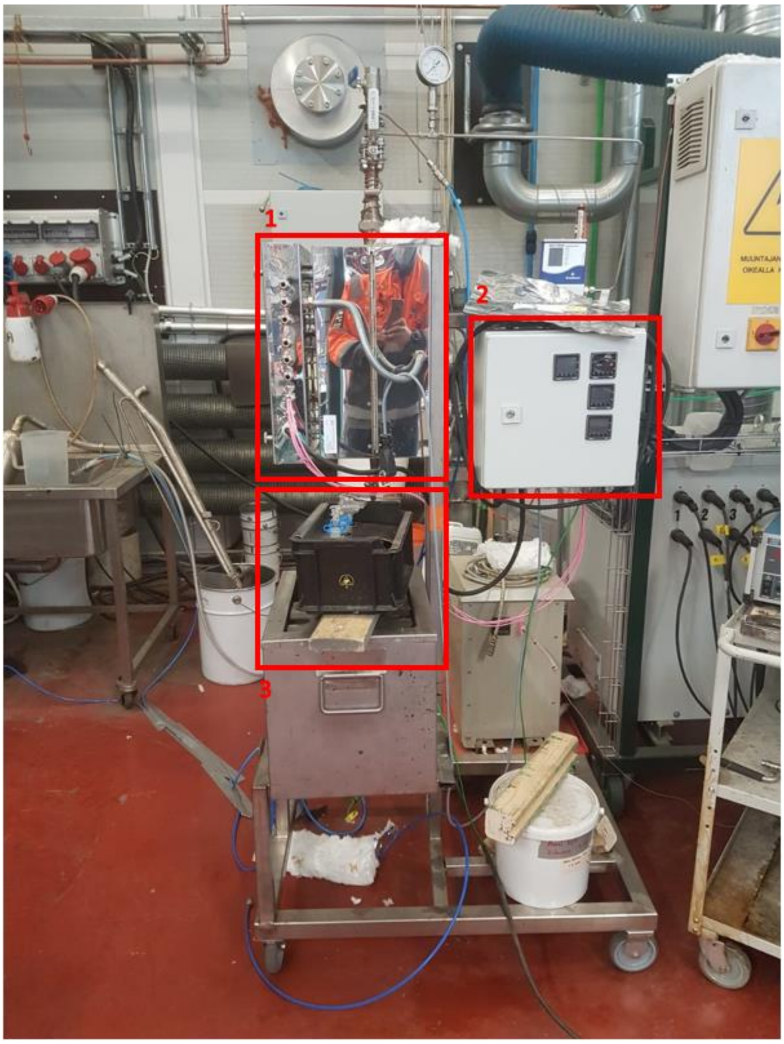


Figure 15. A lab-scale batch reactor unit. 1) Reactor, 2) Temperature control panel, 3) Sample collection section.

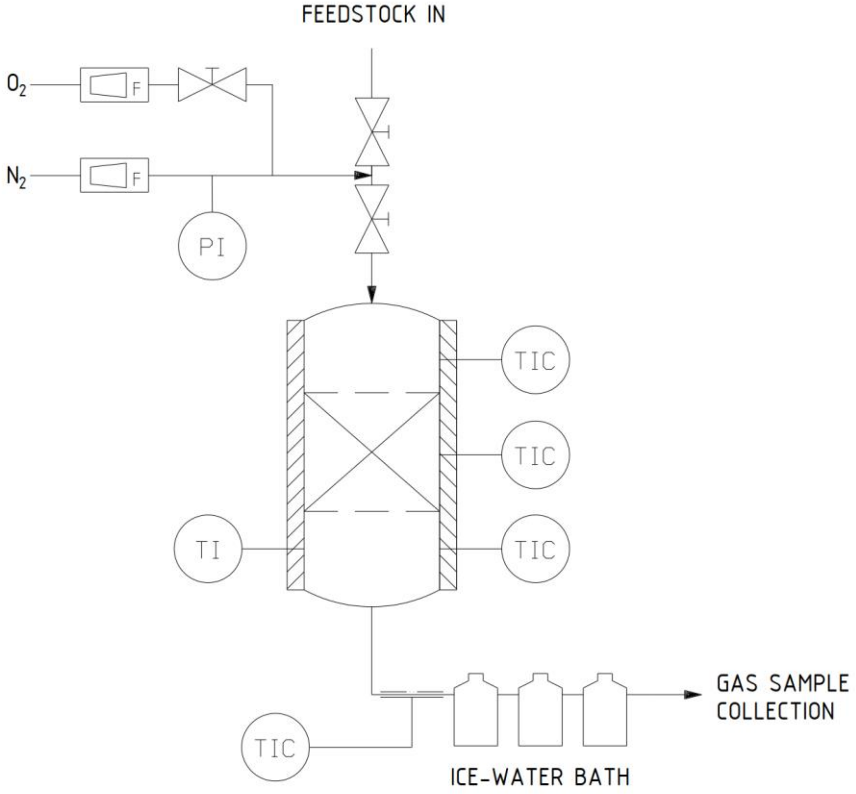


Figure 16. P&ID of the batch reactor.

7.3.2 Fluidized-bed reactor (KILO)

The bench-scale fast pyrolysis unit (referred to as KILO) is a bubble fluidized-bed reactor with a maximum capacity of 1 kg/h. The system consists of feeding tank, reactor, solid separation (two cyclones), and product collection. Liquid products are collected from five different lines. The order for condensing units is water cooler, electric precipitator, glycol cooler and two dry ice coolers. Gas samples are taken at the tail section of the unit hourly. Process block diagram is presented in Figure 17.

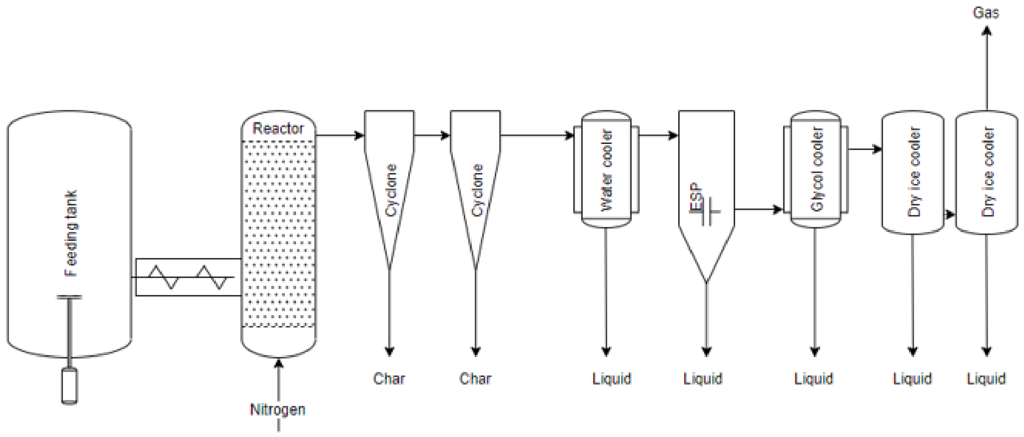


Figure 17. Block diagram of fluidized-bed pyrolysis reactor unit.

7.4 Experimental plan

BR experiments were planned based on literature review and KILO experiments from the results of BR runs. The aim of BR runs was to screen different catalysts and conditions to find the best yield for diesel-range fuel. Chosen catalysts for BR runs were:

- ZSM-5 catalyst
- Montmorillonite (clay) catalyst
- γ-alumina catalyst

Thermal runs were also executed in same temperatures. Temperature was planned to be tested in range 450–500 °C in 50 °C intervals yet was later changed to 500–550 °C in 25 °C intervals. The reasoning behind this is explained in Chapter 8.1. In KILO experiments, the best catalyst was chosen and tested in a different reactor configuration. Temperature was varied parameters. Operational constraints of the experiments are presented in Table 14.

Table 14. Operational constraints of the experiments.

BR runs		
Amount of feedstock	5	g
Carrier gas flow, N_2	40	ml/min
Residence time	1	min
Catalyst/feedstock ratio	1:1	
Experiment time	40	min
KILO runs		
Feed rate	500	g/h
Carrier gas flow	9	l/min
Residence time	3	s
WHSV	1.7	h^{-1}
Catalyst	Montmorillonite	
Experiment time	3	h

7.5 Analysis methods

The products were analyzed in VTT laboratory departments. Analysis done for this thesis is presented in Table 15.

Table 15. Analysis plan for the pyrolysis products.

Analysis	Liquid	Wax	Gas
GC/MS	Yes	Yes	No
GC/FID	Yes	Yes	No
μGC	No	No	Yes
Simulated distillation	Yes	No	No

Liquid characterization analysis was performed with a Shimadzu gas chromatograph equipped with a mass selective quadrupole detector GC/MS-QP2010 Ultra (Figure 18). GC/MS analysis is suitable on the identification of volatile components, especially since in catalytic pyrolysis the product composition can be broad and unknown. The method utilizes sample libraries on the identification of the product from mass spectra and is useful since no model sample is required. In this work it is mainly used on determining to which type of sample are composed of (aliphatic, aromatic, cyclic). It can be used for quantifying the product sample by using internal standard. By knowing the amount of internal standard, the peak areas of internal standard and compounds, the amount of the sample components can be semiquantitatively solved. The calculation method is presented in Equation 5.

$$m_{SAMPLE} = \frac{m_{ISTD}}{A_{ISTD}} * A_{SAMPLE} \qquad (5)$$

Samples for GC/MS were prepared by dissolving the product to tetrahydrofuran (THF). THF is suitable for products with high aliphatic hydrocarbon content whereas 2-propanol (IPA) for high aromatic content products. Sample was initially weighed 30 mg to a 10 ml bottle and filled with solvent. The solution was prepared to a GC vial by adding 950 µl of sample and 50 µl of internal standard solvent. Internal standard solvent was prepared by weighing 20 mg of decyl cyclohexane to a 5 ml bottle and filled with IPA.

Figure 18. GC/MS-QP2010 Ultra System.

For high aromatic content product, i.e. ZSM-5 catalyst runs, GC/FID was used for quantitative analysis of hydrocarbons. An Agilent 6890 Series GC/FID System (Figure 19) was used for the analyses. The analysis measures three calibration points for each component from which the amount of sample can be determined. Sample solution was prepared similarly as with GC/MS with IPA as a solvent instead of THF. n-dodecan was used as internal standard. The solution was diluted to 1:10 and 800 µl of sample and 200 µl of internal standard was measured to a 1 ml vial.

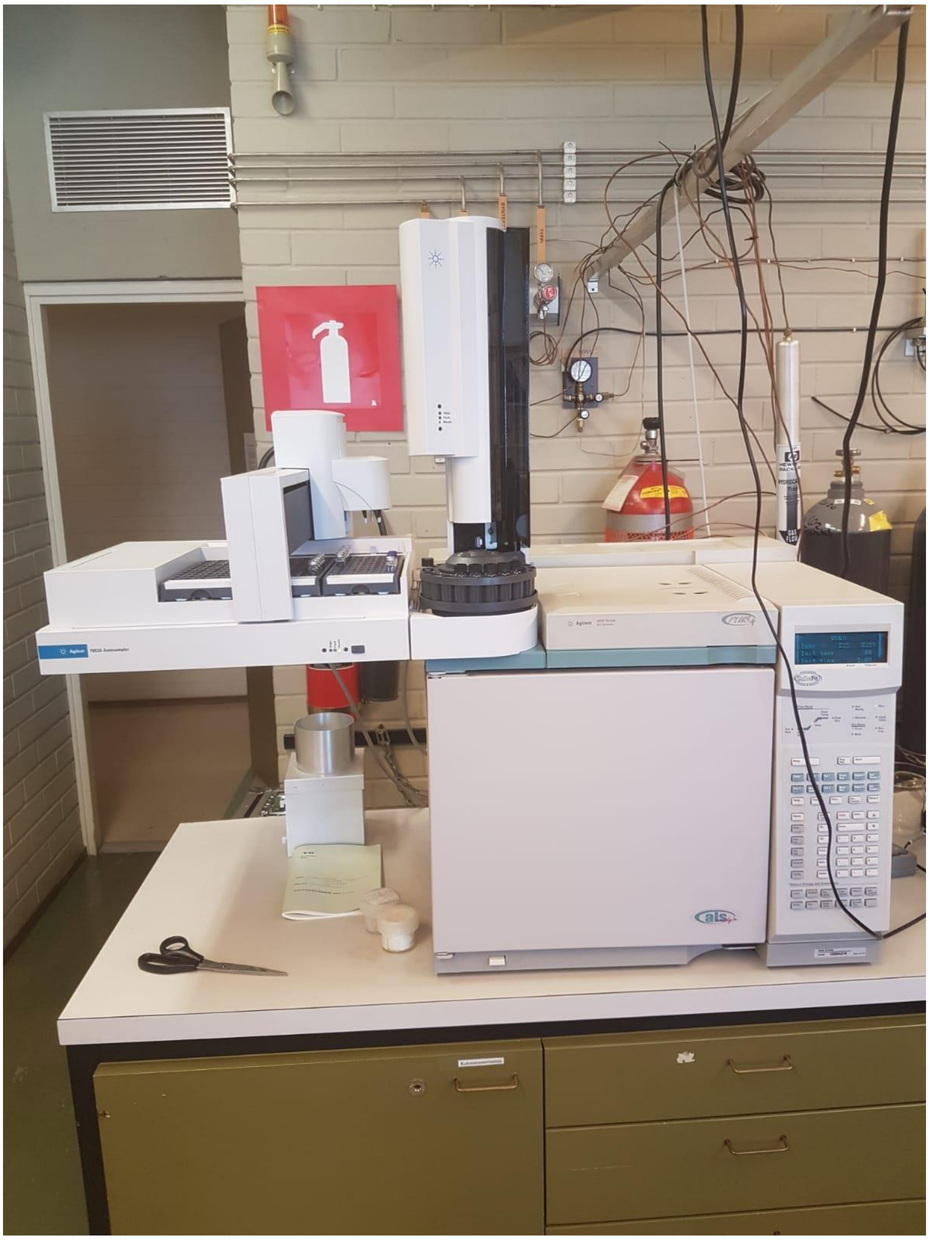


Figure 19. GC/FID for aromatic content analysis.

GC/FID analyzer was used for determining the carbon chain length of hydrocarbons which are in a form of wax at room temperature. A Shumadzu Nexis GC-2030 Gas chromatograph with an on-column inlet and a CP-SimDist UltiMetal high temperature metal-capillary column was used for the analyses (Figure 20). Analysis gives the carbon chain length in groups of $>C_{10}$, C_{11}–C_{17}, C_{18}–C_{37} (light wax) and greater then C_{37} (heavy wax). GC/FID analysis is not intended to give whole product spectrum (since $<C_{10}$ components cannot be determined) but rather to give a good estimation on the ratio between two carbon length fractions (e.g. C_{11}–C_{21} and C_{22}–C_{37}).

GC/FID analysis was done by preparing 10 mg of sample to 1.5 ml of carbon disulphide.

Figure 20. GC/FID.

8 Results and discussion

In this chapter, results and discussion from each experiment are presented. The chapter is divided into two sections where BR and KILO experiments are addresses separately. Results include mass balances, gas composition and liquid analysis such as GC/MS, GC/FID and simulated distillation.

8.1 Batch reactor experiments

Batch reactor (BR) experiment results are presented below.

8.1.1 Mass balance

The results of the BR experiments are presented in Table 16.

Table 16. Summary of BR experiments.

Run	**T [°C]**	**Catalyst**	**Yield [wt. %]**				
			Wax	Liquid	Gas	Solid	Tot
1	500	No	96.6	0.0	1.1	2.3	107.3
2	525	No	88.6	0.0	6.4	0.5	98.6
3	550	No	87.2	0.0	12.5	0.7	100.4
4	500	ZSM-5	0.0	42.0	108.3	0.9	151.2
5	525	ZSM-5	0.0	32.6	71.7	0.2	104.5
6	550	ZSM-5	0.0	31.2	76.1	0.2	107.6
7	500	Clay	0.0	79.4	11.4	1.1	91.9
8	525	Clay	0.0	78.7	13.4	1.0	93.1
9	550	Clay	0.0	70.0	18.6	1.7	90.2
10	500	γ-alumina	0.0	78.8	10.2	0.8	89.8
11	525	γ-alumina	0.0	75.8	12.7	0.8	89.3
12	550	γ-alumina	0.0	73.0	18.1	0.6	91.6

The results are illustrated in Figure 21.

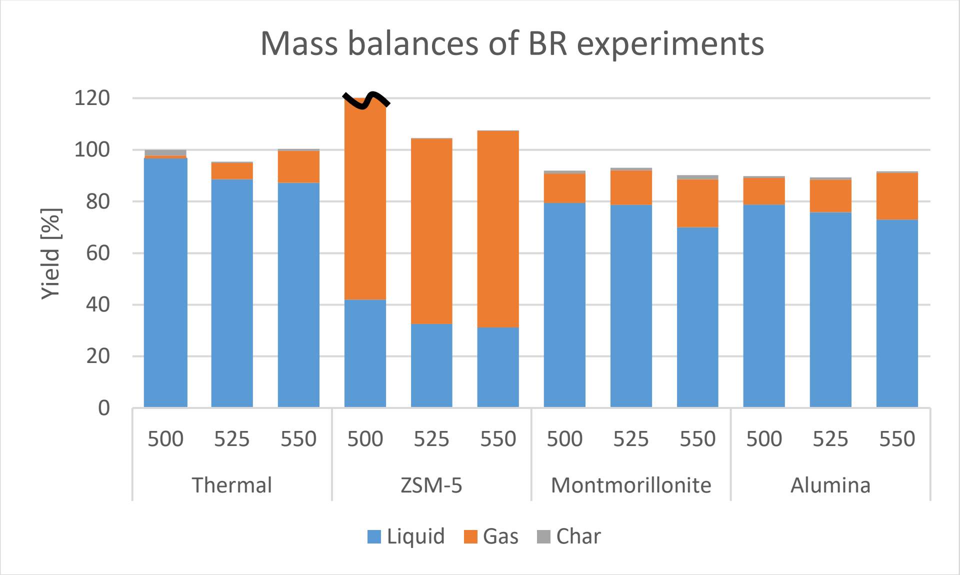


Figure 21. Mass balances of BR experiments.

As mentioned, initial plan included temperature range of 400–450 °C, based on literature survey. 400 °C was not sufficient for the decomposition of the plastic, due to the reactor blockage which occurred as increase in pressure. The reactor temperature was increased to 500 °C and residence time was doubled from 30 s to 60 s which resulted in a successful experiment. Residence time was kept at 60 s for the rest of the runs.

In thermal experiments, the product was a yellowish wax. It drained from the pipeline in melt state to the sample bottles where it solidified on the walls.

As can be seen, ZSM-5 catalyst produced mostly gases. The collected liquid product was a clear yellowish liquid. Due to the high gas composition, an error occurred in gas sample analysis and total mass balance in each ZSM-5 experiments exceeded 100%. One explanation for the inaccurate gas analyses with ZSM-5 is probably the lack of calibration gas with higher hydrocarbon composition. Montmorillonite catalyst resulted in high liquid yield with thick, brownish-like appearance. γ-alumina catalyst produced both liquid and wax in a mixed phase. Distinction between the phases was challenging to make but it was estimated that around half of each were produced. Liquid phase from γ-alumina looked visually clearer than montmorillonite catalyst. The repeated experiment (run #13) was unsuccessful due to the broken gas bag and thus is not included to the results. Products samples are presented in Figure 22.

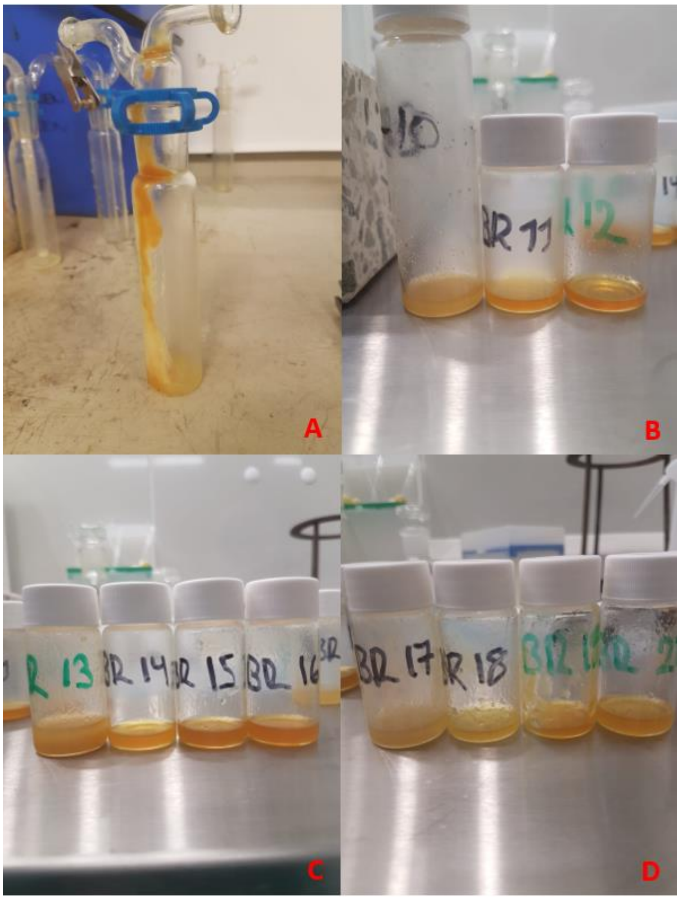


Figure 22. Product samples from BR experiments. A) Thermal run (500 °C), B) ZSM-5 catalyst, C) Montmorillonite catalyst, D) γ-alumina catalyst.

8.1.2 Gas analysis

Gas analysis results are presented below. Most abundant components are taken into the graph (>5 wt.%).

Gas yield from the thermal experiments is presented in Figure 23. The amounts are normalized to 100%.

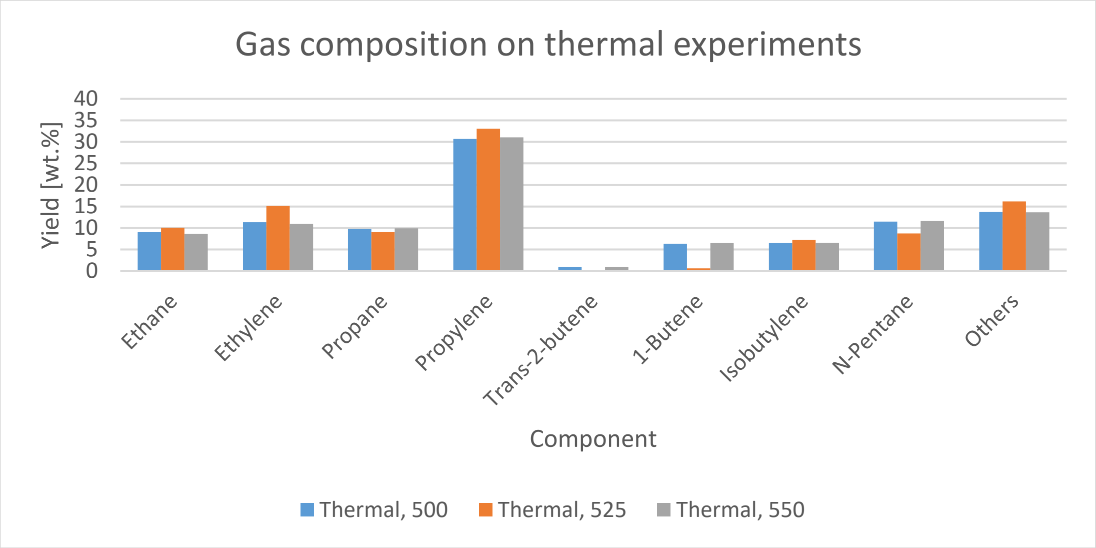


Figure 23. Gas yield on thermal experiments. Amounts normalized.

Propylene accounted around 30 wt.% of the total gas yield. Ethane, ethylene, propane and n-pentane corresponded 10 wt.%.

Gas yield on the catalytic experiments is presented in Figure 24.

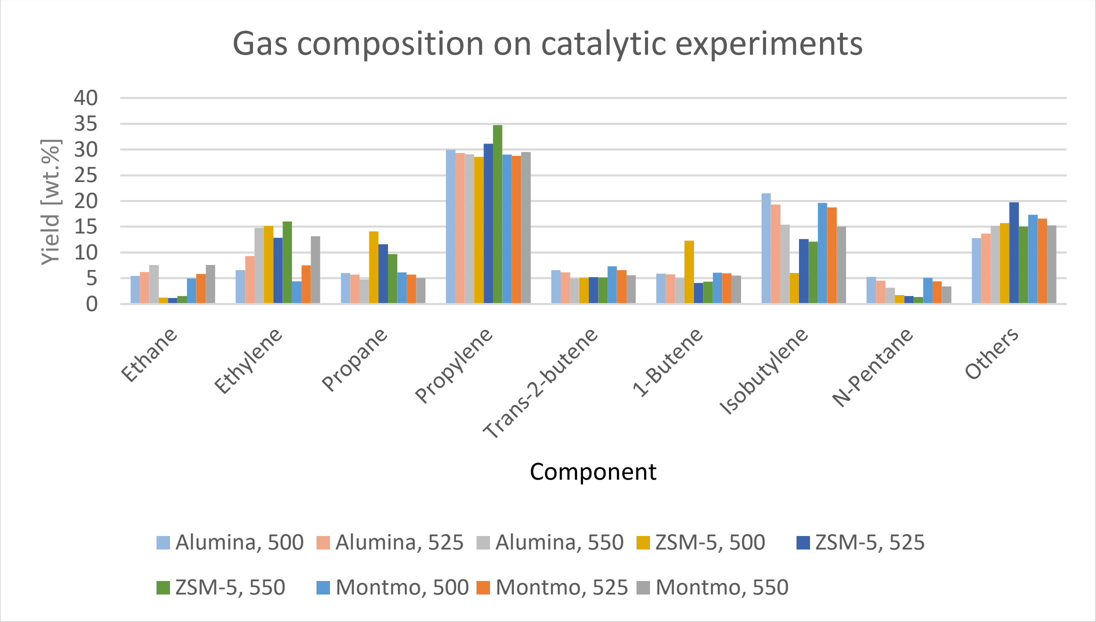


Figure 24. Gas yield on catalytic experiments. Amounts normalized.

Propylene was the most abundant component in the gas phase regardless of the catalyst. Ethylene, propane and isobutylene yield seemed to be affected by the catalyst.

8.1.3 GC/MS and GC/FID analysis

GC/MS analysis data is presented in Appendix 5. In thermal experiments, the products were mostly styrene originated from PS, aliphatic hydrocarbons dienes, alkenes and alkanes from PE and hydrocarbons with methyl branches such as 2,4-Dimethyl-1-heptenes originated from PP feedstock. Summary of carbon length distribution of thermal experiments is presented in Figure 25.

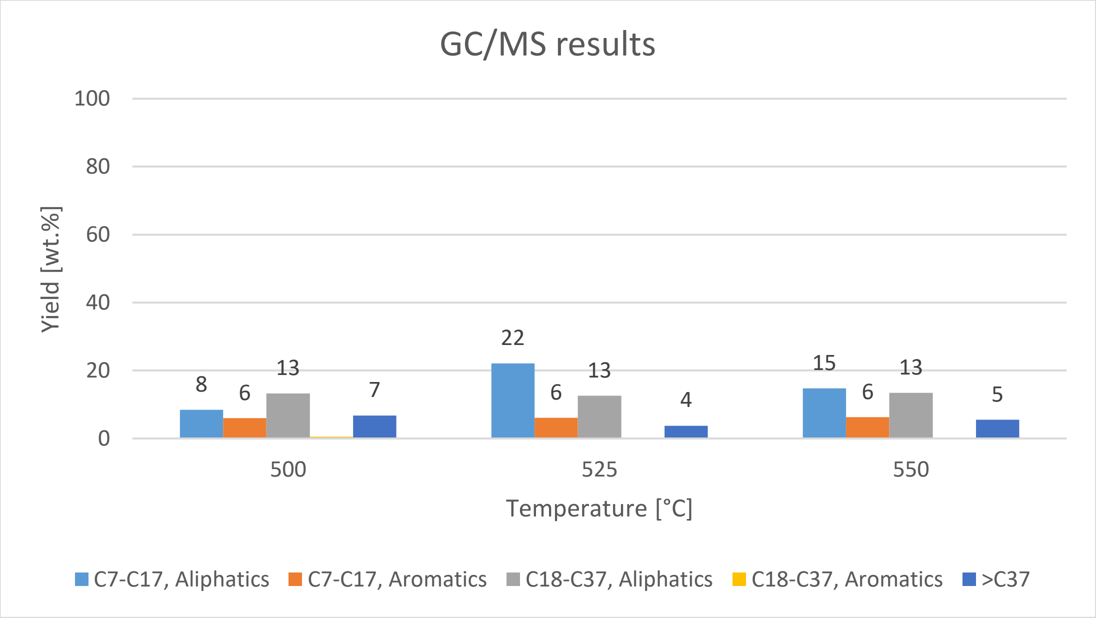


Figure 25. GC/MS results from thermal experiments.

Aliphatic/aromatic ratio was 1.4, 3.7 and 2.4 in temperatures of 500, 525 and 550 °C, respectively.

In the experiments with montmorillonite clay and γ-alumina catalysts, the products included toluene, benzene and styrene as well as major n-alkanes from PE feedstock. The product also included some lighter aliphatic hydrocarbons originated from PP and PE. Temperature did not seem to have major role on the composition of the products. Summary of GC/MS results in carbon length of C_7–C_{17} are presented in Figure 26.

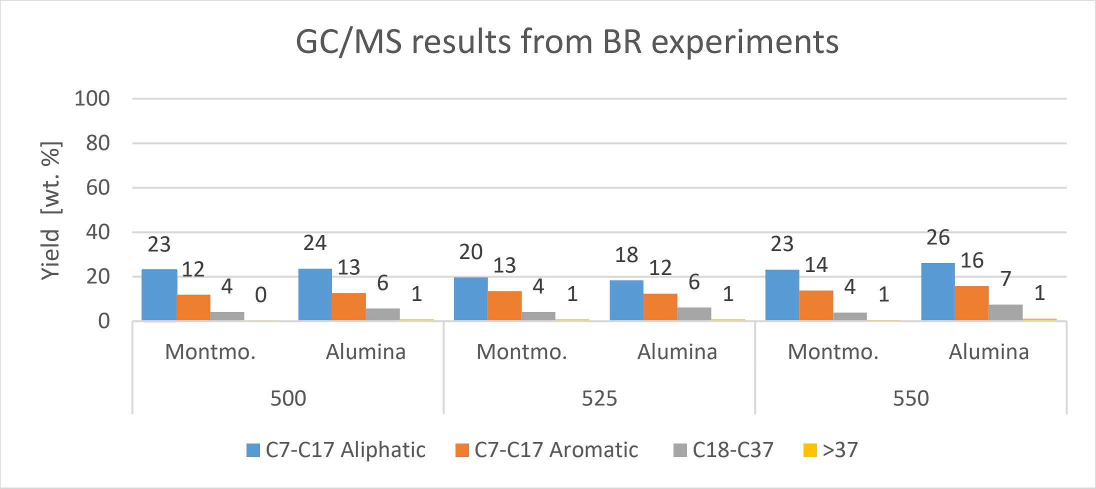


Figure 26. GC/MS summary of catalytic experiments with montmorillonite and alumina.

Weight yield of the products are calculated based on the amount and area of internal standard which is compared to the amount of weighed sample. As can be seen, around 40 wt.% of the products could be quantified in thermal and catalytic runs from GC/MS analysis. Aliphatic to aromatic ratio was 1.5–2 in catalytic experiments.

GC/MS analysis is the most suitable to detect components below C_{40}. More specifically, the products are eluted best in range C_6–C_{37}. Therefore, all compounds present in the oils could not be detected. The aim of GC/MS is to give an estimation on the type of the products in the sample. Therefore, even when the aliphatic and aromatics can be detected from the analysis, the amount of individual aliphatic components might be significantly higher than the analysis result indicates. In addition, the choice of solvent in the analysis can affect the results due to the poor solubility of components.

The experiments with ZSM-5 catalyst yielded high amount of aromatic compounds. The product included mainly benzene, toluene and styrene. Summary of GC/FID analysis for aromatic content concentration is presented in Figure 27.

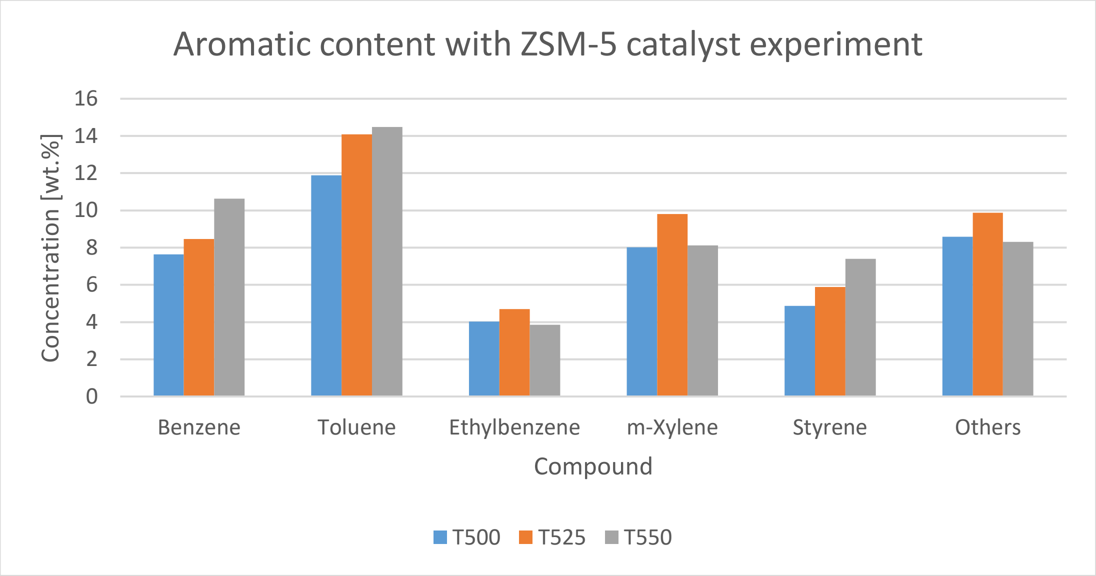


Figure 27. Concentration of aromatic content with ZSM-5 catalyst runs.

Analysis revealed total aromatic yield to be around 50 wt.% in every experiment. It is assumed that rest of the products are aliphatic components.

GC/FID analysis results of the liquid products are presented in Figure 28. In γ-alumina experiments the product included a mixture of liquid and wax. It was not possible to separate the wax from the sample due to the partially liquified appearance. Therefore, some of the wax products are bound to be included in the analysis results of γ-alumina experiments.

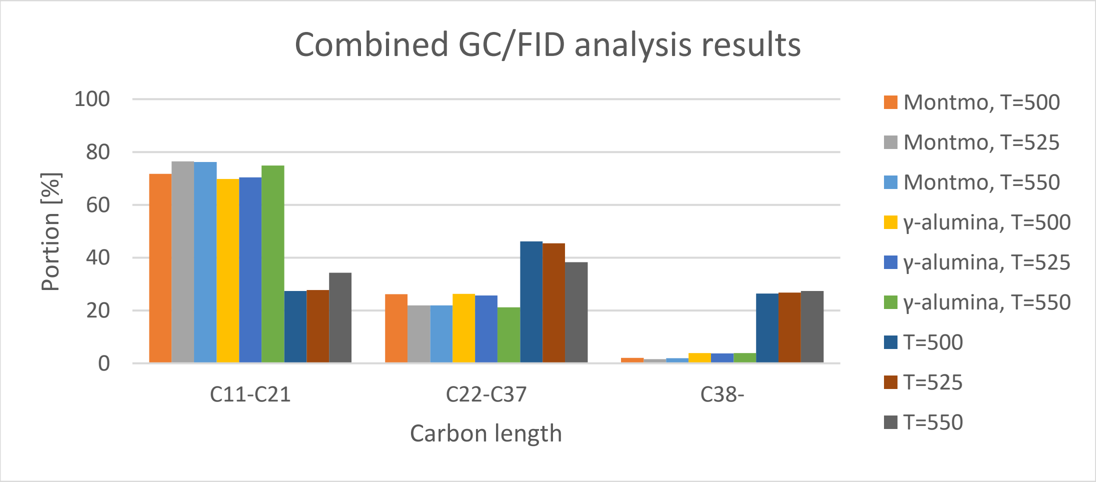


Figure 28. GC/FID analysis of the experiments.

The y-axis represents the portion of the peak areas. As can be seen from the graph, the presence of catalyst greatly shifts the product distribution towards diesel range. In thermal experiments most of the products were in heavier range (wax). Catalysts seemed to yield similar portion of diesel range. The increase of temperature had positive effect on the diesel range yield although the increase was not significant in each case. Important to note is that this method does not show the composition of carbon length shorter than C_{10}. An estimation of these components can be drawn from the simulated distillation curve.

8.1.4 Simulated distillation

Simulated distillation of BR experiments is presented in Figure 29.

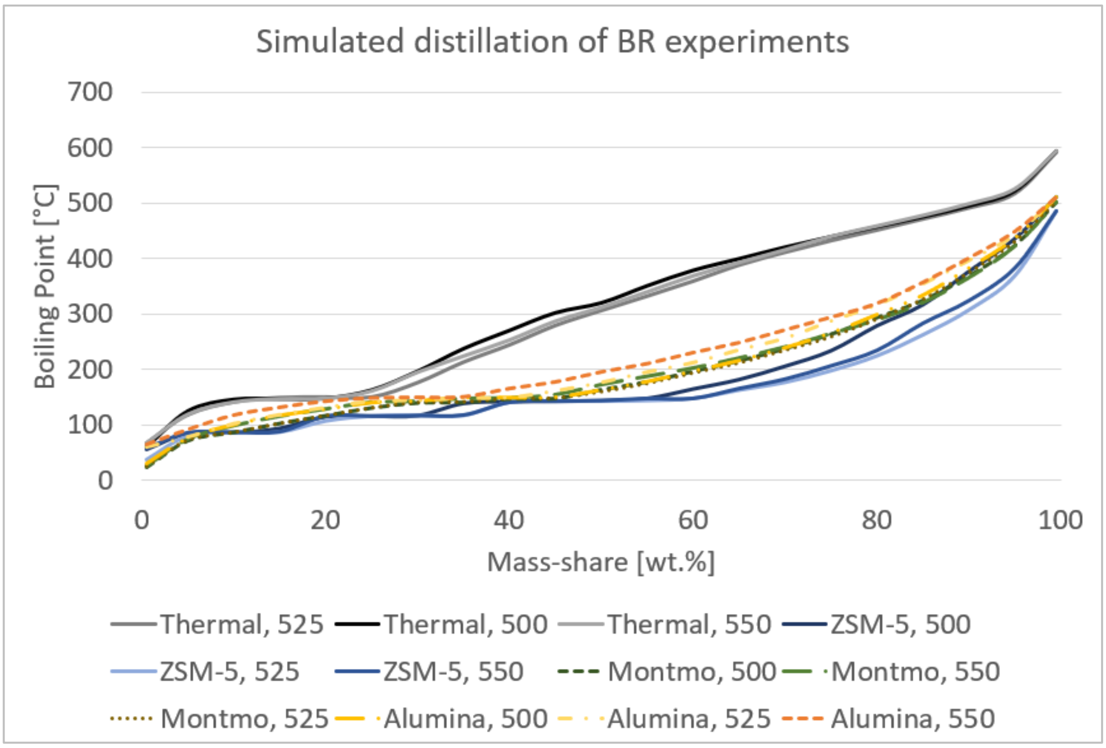


Figure 29. Simulated distillation results from BR experiments.

Clear shift is visible with the presence of catalyst. Boiling point temperature curve is highest in an absence of catalyst which results to thermal pyrolysis produce heavier products. ZSM-5 catalyst seems to yield lighter product than other catalysts. Temperature within this range does not affect the product boiling point significantly. Boiling point range of the products is around 50–600 °C. Boiling point of C_{10} hydrocarbons begins at T=185 °C which results that approximately 40–45 wt.% of the products falls to this range with montmorillonite and γ-alumina catalyst. With thermal experiments the portion accounted 20 wt.% and with ZSM-5 catalyst 55–60 wt.%. This gives the approximation of the amount of the products which are not detected by GC/FID analysis.

It was decided at the beginning of the experiment that residence time was tried to keep relatively short to simulate KILO conditions. Residence time was kept constant with all catalyst so that experimental matrix can be kept within tolerable range. It is not known how the increase of residence time would have influenced to the product quality. In the future, the residence time should be tested in wider range, e.g. shorter residence time with ZSM-5 catalyst or longer residence time in thermal experiments.

8.2 Fluidized-bed reactor experiments

Results from fluidized-bed reactor (KILO) experiments are presented below.

8.2.1 Mass balance

Mass balances of KILO experiments are presented below (Figure 30).

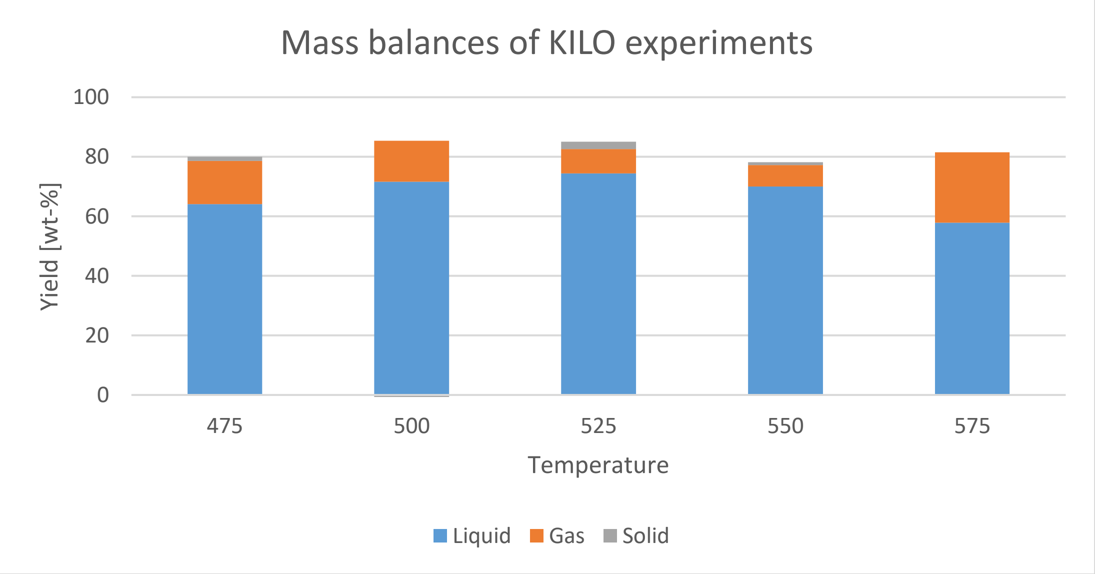


Figure 30. Mass balances of KILO experiments.

Average mass balance in the experiments was around 80 wt.% which is typical for the used unit. A proposed explanation for the loss of product could be that volatile products which are not detected in gas analysis escapes from the collection unit.

Average liquid yield was 70 wt.%. Colour of the product was black, and the viscosity resembled a fuel (Figure 31). No wax was formed in any of the experiments.

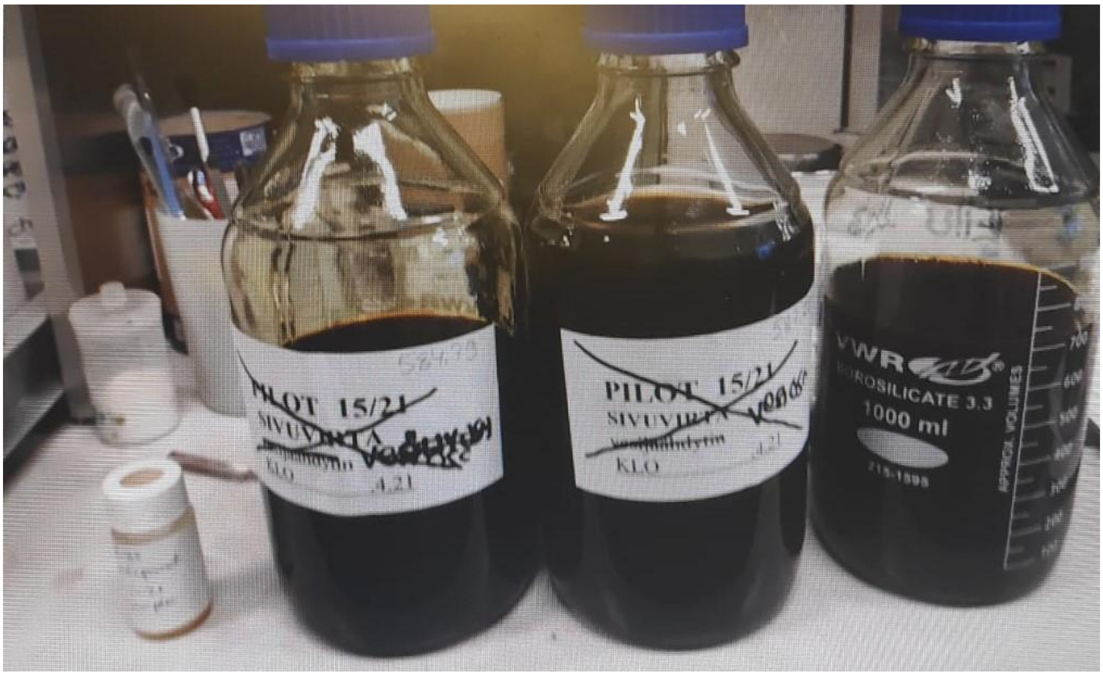


Figure 31. Products from KILO experiment.

CHN analysis was performed to the catalyst bed after the experiment. The results are presented in Figure 32.

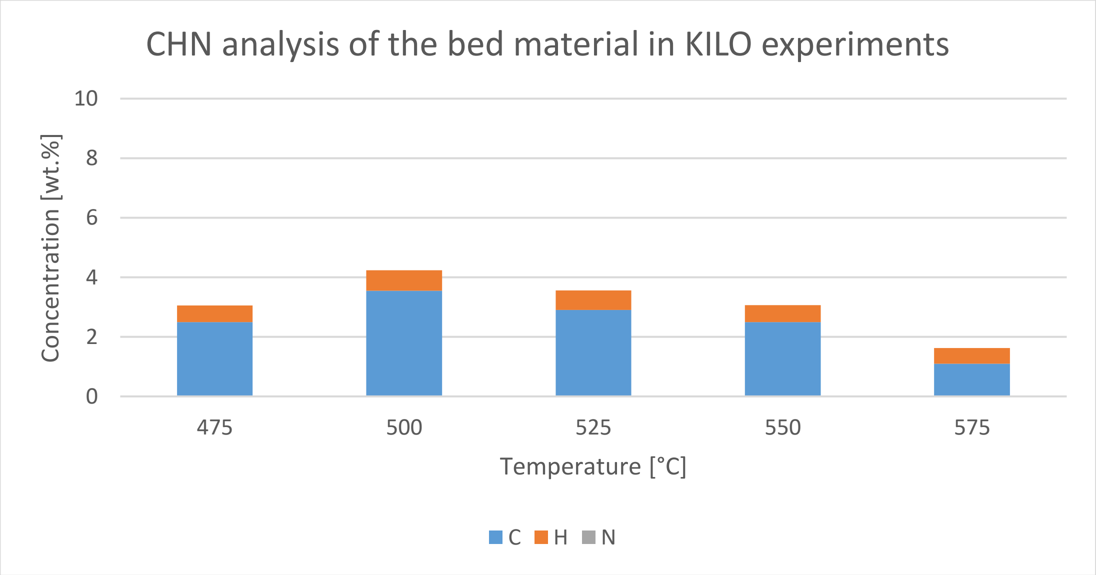


Figure 32. CHN analysis from the KILO experiments.

Coke formation has similar trend as with liquid yield (Figure 30). Increase of temperature reduces the amount of coke in the bed. BET surface area analysis was also performed to the used catalyst bed. The results are presented in Figure 33.

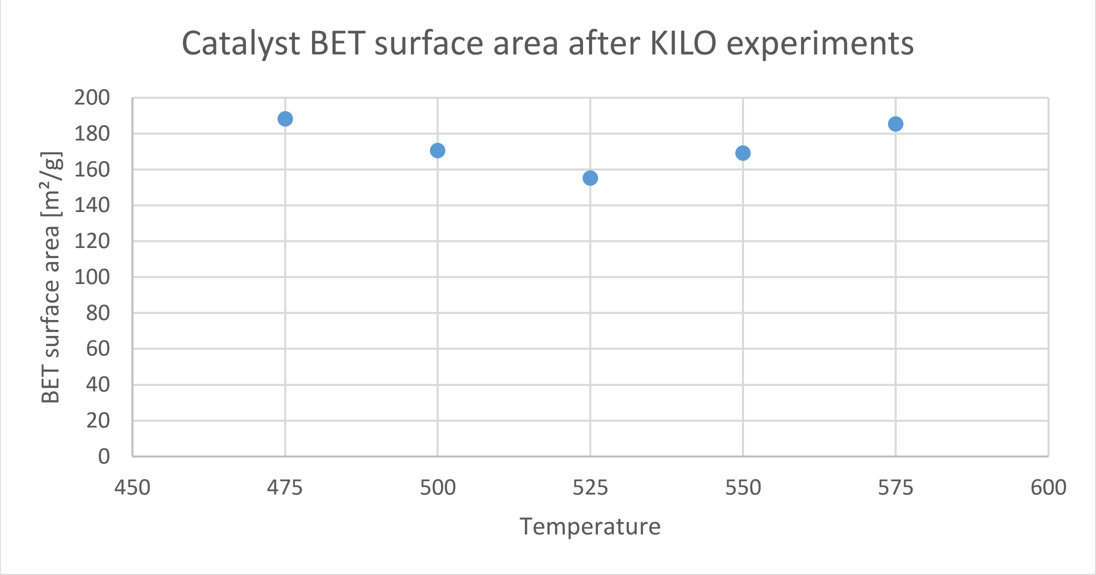


Figure 33. BET surface areas of the catalyst bed after the experiment.

The graph shows that the curve has parabolic behavior and the lowest BET area is achieved in T=525 °C. The values at the temperature limits are approximately same. As a reference, unused catalyst bed BET surface area was 228 m²/s. This means that after three hours experiment the BET surface area reduced by 32% at T=525 °C and by 17% at T=475 °C.

8.2.2 Gas analysis

Gas analysis results from KILO experiments are presented in Figure 34.

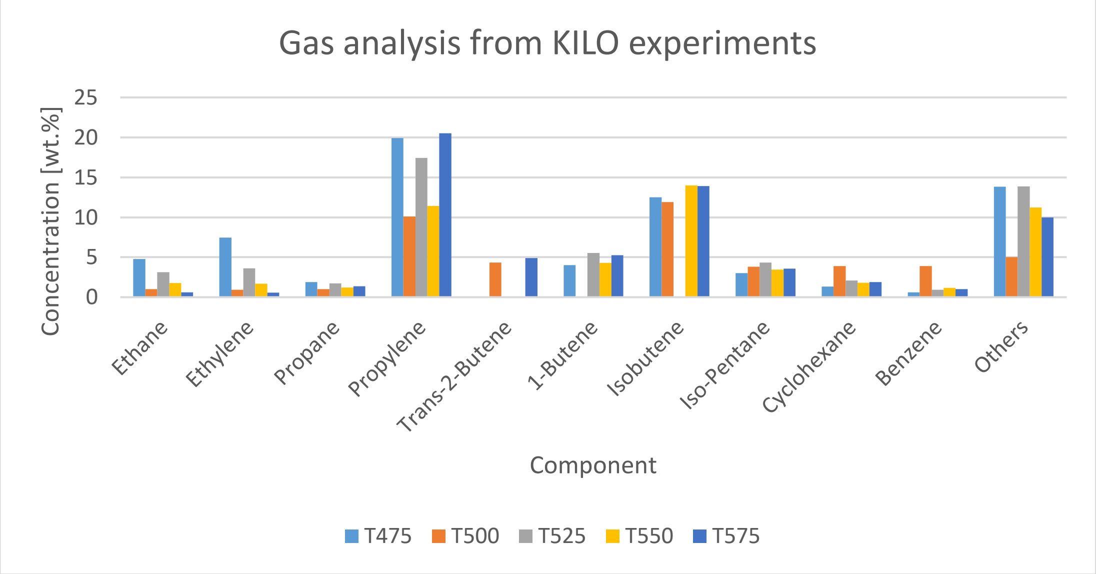


Figure 34. Gas product concentration from KILO experiments.

As can be seen, propylene is the most abundant component in the gas sample. Some components are absent in a few experiments which can be an analysis error. As said, gas samples were taken twice one hour apart which can cause inaccuracy to the results if the gas composition is not homogeneous throughout the experiment.

8.2.3 GC/MS and GC/FID analysis

GC/MS analysis results from KILO experiments are presented in Figure 35.

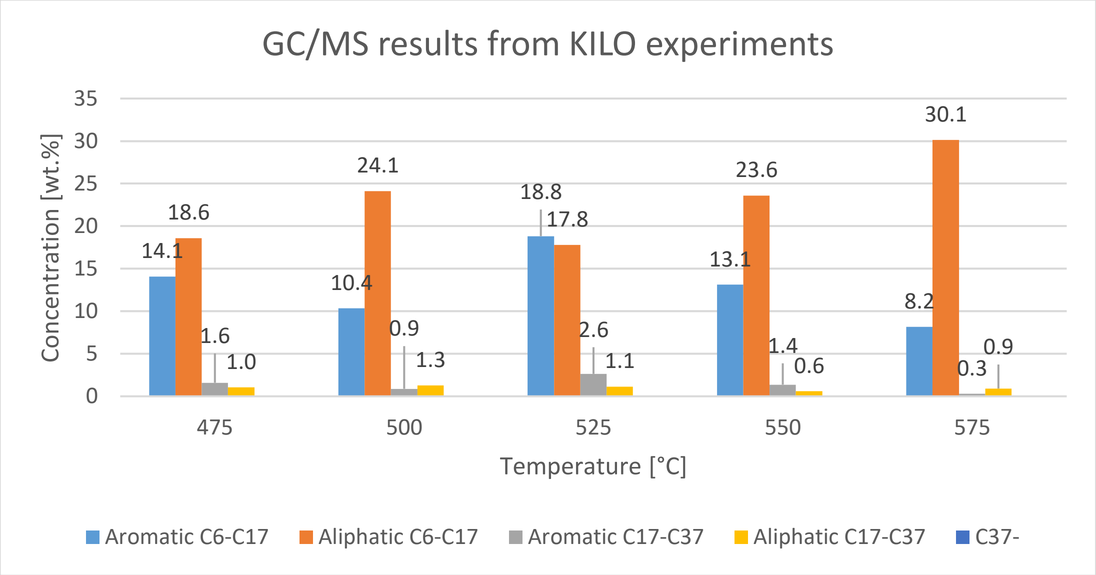


Figure 35. GC/MS analysis results of KILO experiments.

GC/MS analysis accounted 30–40 wt.% of the products. Based on the results, the increase of temperature has a positive effect on the composition of aliphatic in range of C_6–C_{17} fraction. The peak is in temperature of 575 °C which was the highest tested temperature. There is one abnormal point at T=525 °C where the portion of aromatics exceeds the amount of aliphatic. It is challenging to state which causes this phenomenon and it may be a simple analysis or sample preparation error. Aliphatic/aromatic ratio in the experiments was 1.3, 2.3, 0.9, 1.7 and 3.7 in 475, 500, 525, 550 and 575 °C, respectively. GC/MS analysis revealed over 240 components in a range of C_6–C_{17}. The most abundant individual components were benzene, 2-Methyl-2-hexene, toluene, 4-Octene, ethylbenzene, styrene, 1-Ethyl-2-methylbenzene and indane. Abovementioned components accounted 20–30 % of the peak areas in GC/MS analysis. Product composition from GC/MS analysis is presented in Figure 36.

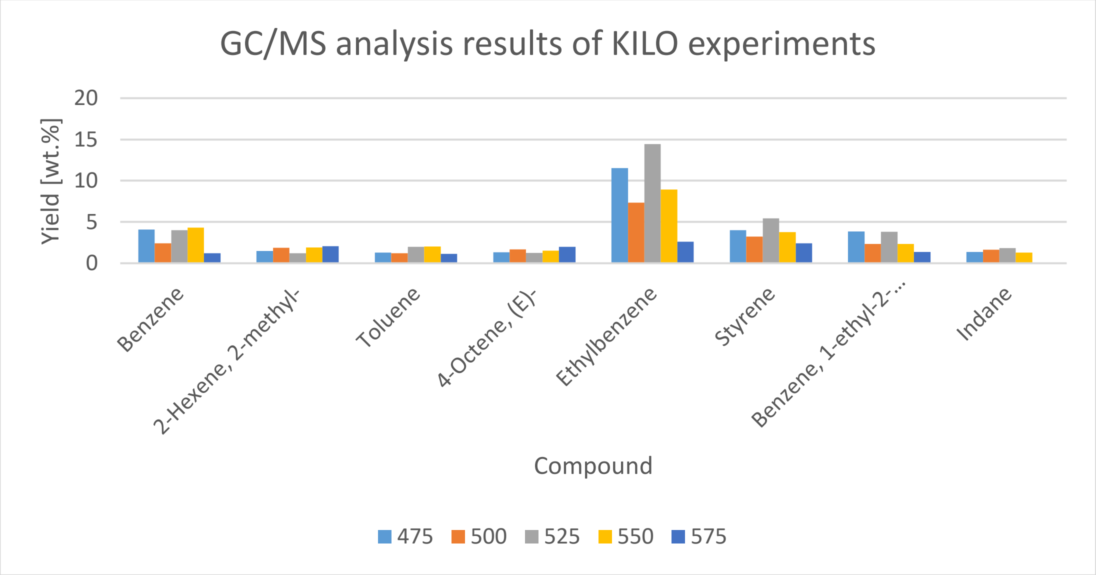


Figure 36. GC/MS analysis results of KILO experiments. Product composition.

GC/FID analysis from KILO experiments are presented in Figure 37.

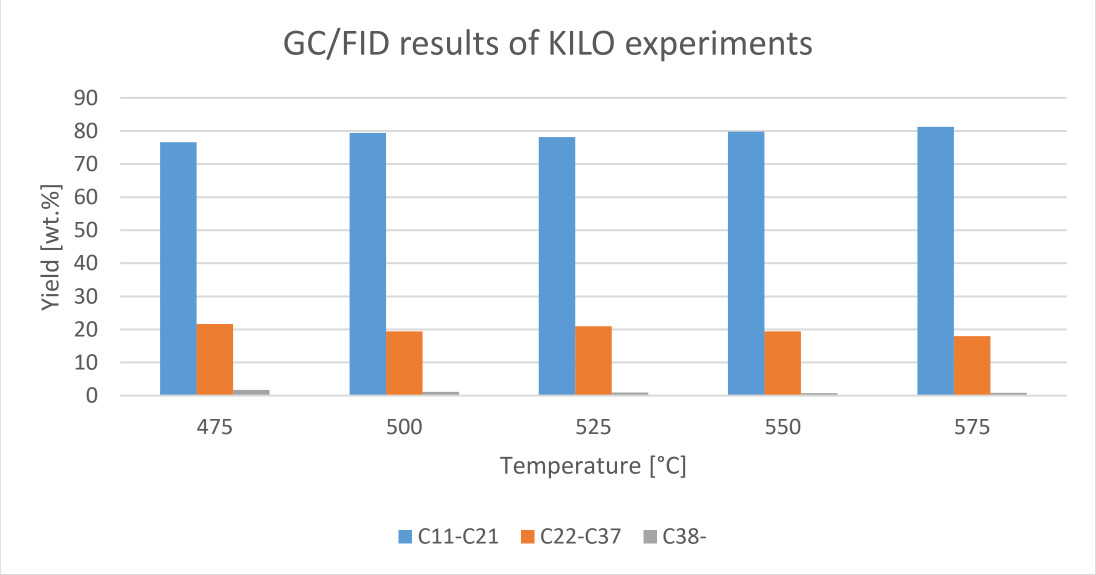


Figure 37. GC/FID analysis of KILO experiments. Normalized results.

Most of the detected products are in carbon length of C_{11}–C_{21}, which falls to diesel range. Around 20% of the product corresponded to a heavier fraction (C_{22}–C_{37}). The results are normalized since no quantitative analysis can be done due to the inability to analyse components with carbon length of C_{10} or less with this method.

Aromatic content was also determined with GC/FID analysis. Weight yield is presented in Table 17.

Table 17. Aromatic content from KILO experiments.

T [°C]	Aromatic content [wt.%]
475	13.5
500	15.4
525	14.4
550	17.6
575	9.8

The most abundant components from the analysis are presented in the Figure 38.

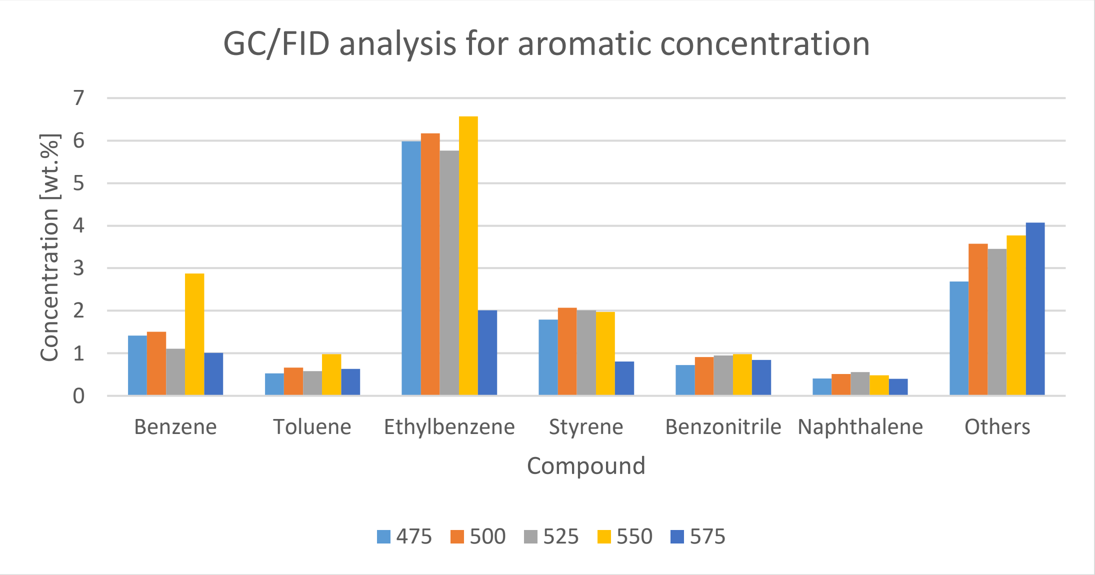


Figure 38. GC/FID analysis to determine the aromatic content.

Aromatic content resembles the analysis results from GC/MS. The composition of the sample included mostly ethylbenzene (4–6 wt.%) and styrene (1–2 wt.%). The formation of styrene can be expected to originate from PS feedstock.

8.2.4 Simulated distillation

Simulated distillation results are presented in Figure 39.

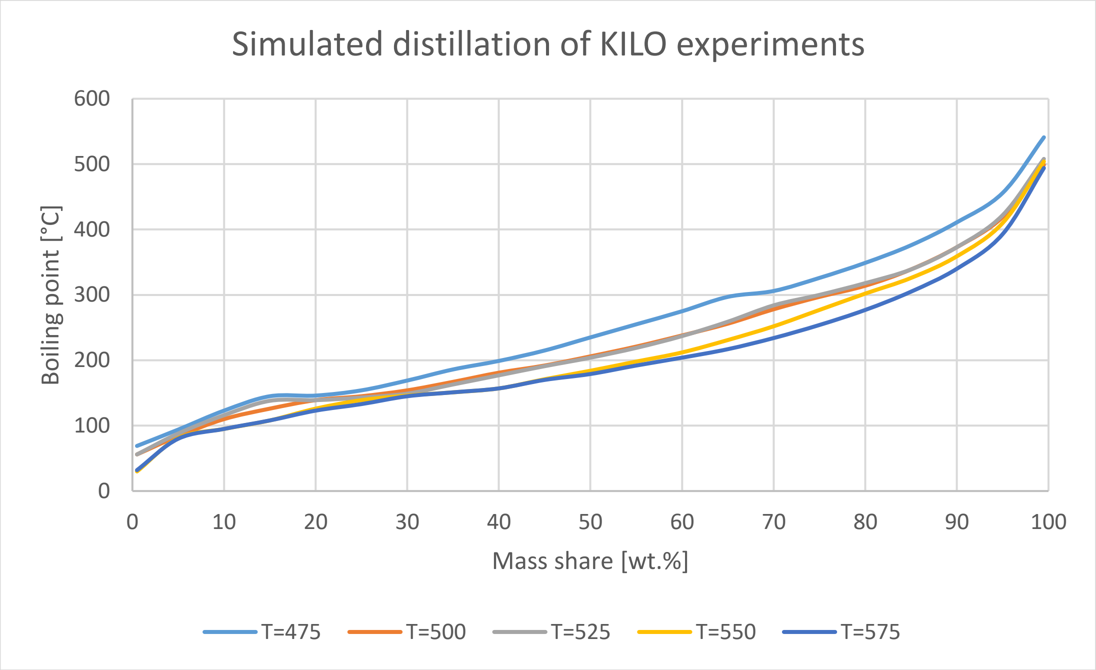


Figure 39. Simulated distillation from KILO experiments.

As can be seen from the graph, the difference among the products is not significant. A slight shift towards lighter components is present when temperature is increased. T=575 °C has the lowest boiling temperature curve whereas T=475 °C the highest. Components with C_{10} or less corresponded 25–35 wt.% based on the curve. As mentioned in Chapter 3.1, marine diesel oil RMB standard has a boiling point range of 180–570 °C. In Figure 40 the comparison between the products and RMB marine diesel oil in terms of acceptable boiling point range is presented. The percentage represents on how large portion falls in this range.

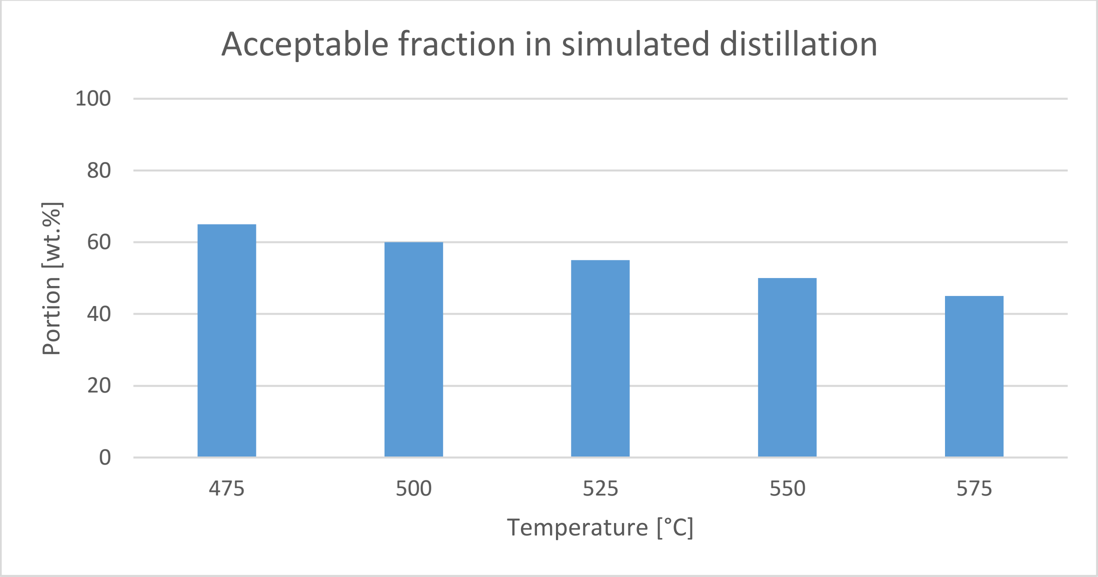


Figure 40. Comparison of the product and RMB marine diesel oil boiling point ranges.

Based on the analysis, lower temperatures increase the portion of diesel range product.

It was noted during the analysis that there is not one uniform analysis method which reveals whole product distribution. The liquid/wax produced from pyrolysis includes large spectra of different sort of components in a broad carbon length. Same procedures cannot be used with lighter components and with wax products. GC/FID is suitable for heavier components. In fact, it was initially designed for wax analysis. GC/MS is suitable for product identification but can be problematic if product needs to be diluted over to certain degree. It was noted that some components were not identified since the weight yield in GC/MS in BR experiments was only 50 wt.%. Simulated distillation was useful to give the most accurate estimation on the whole product distribution. This along with the other analysis methods yields a good approximation on the product quality, quantity and boiling point range.

9 Conclusion and proposal for future work

In the modern era, recycling and utilization of alternative raw materials are becoming increasingly important topics. Plastic is annually consumed at an accelerating rate which requires actions to find processes for the management and utilization, especially due to the high potential in energy content. Pyrolysis offers an alternative way to convert feedstock to more suitable products via thermal degradation. Feedstock composition is an important factor when considering the product quality. More specifically, the presence of impurities which can produce harmful compounds on the process needs to be considered. Pyrolysis can be practiced with or without the presence of catalyst, yet selecting appropriate catalyst is important to the quality of the product and desired product. Other factors such as temperature, residence time, reactor type etc. also contribute to the end result. Many upgrading methods for pyrolysis product are researched such as distillation, hydrogenation, dewaxing etc. which are mostly inevitable for the product to be used in diesel engine.

In this work, the objective was to find a route to produce diesel fuel suitable for marine engines from polyolefin feedstock. Literature research was carried out on the subject in order to find the best parameters on producing diesel range fuel. It was found that the presence of catalyst and right conditions are fundamental factors on product range distribution. Catalyst with large pore size and low acidity tends to yield more heavier fraction than small pore size and high acidity. Additionally, diesel range fuel favors moderate temperatures with longer residence time. Reactor type must be chosen accordingly to optimize contact mode of the feedstock with catalyst and ensure sufficient residence time of the reaction. Many post processing options for the product are available and must be chosen based on the desired result.

The thesis included experimental work where different catalysts and conditions from literature were put in practice in VTT pilot facilities. The work was divided into two sections: catalytic screening and bench-scale pyrolysis tests. In catalytic screening, catalysts were tested in lab-scale batch reactor. Three different catalysts were tested in three temperature points. Results showed that ZSM-5 catalyst yielded a high amount of gases and aromatic components whereas montmorillonite catalyst and γ-alumina catalyst yielded liquids within diesel range. Thermal experiments produced mainly wax. With montmorillonite and γ-alumina, most of the products were in a range of C_{11}–C_{21} and aliphatic/aromatic ratio was in range of 1.5–2. Simulated distillation revealed that the proportion of lighter components ($<C_{10}$) was significantly affected by the presence of catalyst. Montmorillonite catalyst was chosen for further experiments with a bench-scale fluidization unit. Varied parameter in the experiments was temperature, approximately within same range as in lab-scale unit. The results showed that temperature did not seem to have significant effect on the liquid yield, although some reduction was observed at higher temperatures. Average liquid yield was 70 wt.% with no detectable wax formation. GC/MS analysis revealed that temperature had some effect on quality of the product, where the increase of temperature had positive effect on the yield of aliphatic compounds. Most of the products were in boiling point range of 50–550 °C, based on simulated distillation. C_{10} and lighter components accounted for 25–35 wt.% of total mass share. Lower temperatures favored the formation of heavier components, based on the simulated distillation. At temperature of 475 °C the portion of acceptable fraction accounted around 60 wt.% and at 575 °C around 40 wt.%. GC/FID analysis showed similar results as BR runs where most of the detected products were in range of C_{11}–C_{21} (>70 %), compared to heavier fraction. Detected aromatic compounds corresponded 15–20 wt.% of the total liquid product.

In conclusion, pyrolysis of polyolefins is a tempting process choice to achieve desirable product when suitable catalyst is deployed. In this work, pure plastics were which ignores all the problems generated by impurities in the feed. This is especially important factor when considering the catalyst behavior. In the KILO experiments catalyst BET area decreased third in three hours in T=525 °C. More tests should be carried out in order to see the catalyst behavior in longer experiments or with the presence of impurities. For the pyrolysis of polyolefins to be industrially viable option, more tests need to be done in pilot scale and the issues faced with detrimental components needs to be addressed when real plastic waste is pyrolyzed. The temperature and residence time should be tested in wider range to see the maximum yield for the diesel range product. Additionally, analysis of the plastic pyrolysis product is a challenging task since there is not a standardized method to identify and quantify the product. Marketing and commercializing the process requires the product to be under standardization. Analysis of the product revealed product distribution, composition, share of aromatics and boiling point range. More tests need to be performed such as engine tests, properties (e.g. cetane number, cloud point) and stability tests for more thorough understanding of the product and usability in diesel engines.

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Appendix 1. A summary of catalytic pyrolysis of polyolefins.

Feedstock	Catalyst	Reactor type	Temperature [°C]	Products [wt.%]				Notes	Ref.
				Gas	Liquid	Wax	Solid		
PE:									
HDPE	No	Batch reactor	420–440	9	74		17	Primarily saturated aliphatic paraffinic hydrocarbons (94.0 wt.%). Product was distillated to 4 fractions, medium T fraction (290–340 °C) met EN590 specs with additives added	(54)
PE	No	Batch reactor	450	62	0	25	13		(41)
HDPE	ZSM-5	Batch reactor	450	64	35		1	Mostly in gasoline range	(59)
	USY zeolite			27	72		1	Mostly in gasoline range	
	Mordenite			19	79		3	30 wt.% in diesel range by weight	
	Silica-alumina			21	78		1	Mostly in gasoline range	
	Alumina			16	82		2	Highest yield on diesel range hydrocarbons	
HDPE	FCC	Batch reactor	450	6	82		11	Diesel range hydrocarbon yield was highest at T=450 °C. Not significant difference among catalysts	(57)
	HZSM-5			15	81		4		
	Clinoptilolite containing rhyolite			6	79		15		
HDPE	ZSM-5	Tube extruder	520	12	69		19	34.5 wt.% in gasoline range, 24.1 wt.% in light oil range	(60)
PE	USY zeolite	Batch reactor	450	27	71		2	Peak at carbon length C_{10}-C_{13}	(83)

HDPE	FCC, ZSM-5, clinoptillonite	Batch reactor	410–450	5	70–75		5–10	Not significant difference among catalysts	(58)
HDPE	HZSM-5	CSBR	500	0–58	0–50	0–38		Vapor-phase catalysis. Catalyst space-time was varied which affected significantly to distribution. Diesel range highest w/o catalyst	(34)
HDPE	HUSY zeolite	Batch reactor	550	40	41		2		(84)
LDPE				34	62		2	LDPE yielded mostly n-paraffins and HDPE iso-paraffins	
LDPE	n-HZSM-5	Batch reactor	420	65	35		0	Highest liquid yield was achieved with MCM-41 catalyst with LDPE feedstock	(62)
	HY zeolite			8	19		73		
	amorphous silica-alumina			5	21		74		
	activated carbon			5	9		86		
	Pd charcoal powder			5	10		85		
	MCM-41			12	47		41		
PE	USY zeolite	Continuous vertical reactor	500	25	74		1	Light molecules with range C_1-C_{17}, max in C_5-C_7 (34%)	(12)
LDPE	Flyash	Batch reactor	500	30	16		54	Higher liquid yield w/o catalyst with this setup. Liquid quality better with catalyst	(85)
	Zeolite			28	15		57		
LDPE	No	Screw kiln	500	4	82	14	0	55.6 wt.% C_{13}-C_{33}	(86)
	MCM-41			13	86	12	0	74.2 wt.% C_5-C_{12}	

LDPE	No	Two-step heated quartz vessels	450	16	75	1	0	Selectivities for C_1-C_4, C_5-C_{12}, C_{13}-C_{22} were 16, 41 and 40 wt.%, respectively	(87)
	n-HZSM-5			74	16	1	0	77 wt.% C_1-C_4, gasoline range 23 wt.%	
	Al-MCM-41			58	34	2	0	41 wt.% C_1-C_4, gasoline range 56 wt.%	
HDPE	TiCl3	Tube reactor	430	12	84		4	Very high portion of n-paraffins (80%)	(88)
	HZSM-5			37	60		3	Large amount of aromatics (34 wt.%) and naphthenes (21.7 wt.%)	
HDPE	Clay, montmorillonite	Semi-batch reactor	400	24	72		4	Better liquid yield and heavy fraction compared to USY zeolite	(64)
	Clay, saponite			26	72		2		
PE	SA-1	Batch reactor	430	24	68		9		(67)
	SA-2			13	74		12		
	ZSM-5			44	50		6		
	FSM			11	71		18		
PP:									
PP	No	Batch reactor	450	55	42	0	4		(41)
PP	USY zeolite	Batch reactor	450	17	82		1	Carbon length peak at C_5-C_{11}	(83)
PP	Kaoline	Semi-batch reactor	450	10	90		1	Highest yield at T=500 °C. Product contained olefins, aliphatic and aromatics	(89)
	Silica-alumina		500	8	91		1		
PP	ZSM-5	Semi-batch reactor	350	N/A	89	N/A	N/A	Hydrogenation done with Ni/ZSM-5, complete conversion from alkene to alkanes.	(71)

PP	USY zeolite	Continuous vertical reactor	500	80	19		1	Light molecules with range C1-C15, max at C5-C7 (39 wt.%)	(12)
PP	$AlCl_3$	FBR	400	2	73		25	Liquid-phase. Cat. yield oil frac. (21 wt.%) thermic pyro (35 wt.%)	(90)
PP	SA-1	Batch reactor	430	11	78		10		(67)
	Silicalite			12	75		13		
	ZSM-5			50	47		3		
	FSM			7	86		7	FSM provided heavier hydrocarbons, compared to others	

Appendix 2. EN590 standard for diesel fuel (91).

Property	Value	Unit
Cetane number	≥51.0	
Cetane index	≥46.0	
Density at +15 °C	820.0…845.0, 800.0*	kg/m³
Polycyclic aromatic hydrocarbons	≤8.0	% (m/m)
Sulfur content	≤10.0	mg/kg
FAME-content	≤7.0	% (V/V)
Flash point	> 55	°C
Carbon residue on 10% distillation	≤ 0.30	% (m/m)
Ash	≤0.010	% (m/m)
Water	≤ 0.020	% (m/m)
Total contamination	≤ 24	mg/kg
Copper corrosion	Class 1	
Oxidation stability	≤ 25, ≥20**	g/m³, h
Lubricity HFRR at +60 °C	≤ 460	µm
Viscosity at +40 °C	2.000 … 4.500, ≥1.200*	mm²/s
Distillation 95% (V/V)	≤360	°C
Cloud point and CFPP	Down to -34	°C

*Winter grades

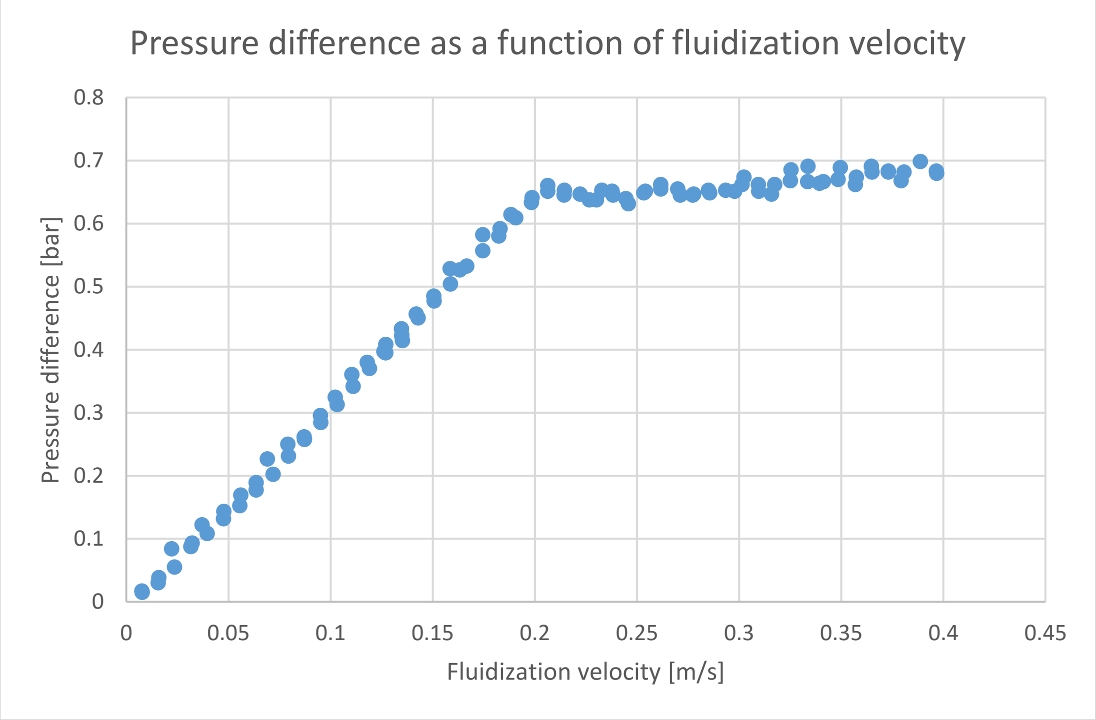
** Additional requirement if contains above 2 vol-% FAME

Appendix 3. ISO 8217 Standard for marine diesel fuel.

Characteristics		Unit	Limit	Category				Test method reference
				DMX	DMA	DMZ	DMB	
Kinematic viscosity at 40 °C[a]		Mm^2/s	Max.	5.500	6.000	6.000	11.00	ISO 3104
			Min.					
Density		Kg/m^3	Max.	1.00	1.50	1.50	2.00	ISO 8754 ISO 14596
Cetane index		–	Min.	45	40	40	35	ISO 4264
Sulfur[b]		Mass %	Max.	1.00	1.50	1.50	2.00	ISO 8754 ISO 14596
Flash point		°C	Min.	43.0	60.0	60.0	60.0	ISO 2719
Hydrogen sulfide		Mg/kg	max.	2.00	2.00	2.00	2.00	IP 570
Acid number		mg KOH/g	max.	0.5	0.5	0.5	0.5	ASTM D664
Total sediment by hot filtration		mass %	max.	–	–	–	0.10[c]	ISO 10307-1
Oxidation stability		g/m^3	max.	25	25	25	25[d]	ISO12205
Carbon residue: micro method on the 10% volume distillation residue		mass %	max.	0.30	0.30	0.30	–	ISO 10370
Carbon residue: micro method		mass %	max.	–	–	–	0.30	ISO 10370
Cloud point		°C	max.	-16	–	–	–	ISO 3015
Pour point (upper)d	winter quality	°C	max.	-6	-6	-6	0	ISO 3016
	summer quality	°C	max.	0	0	0	-6	ISO 3016
Appearance		–	–	Clear and bright			[e,f,g]	
Water		volume %	max.	–	–	–	0.30[e]	ISO 3733
Ash		mass %	max.	0.010	0.010	0.010	0.010	ISO 6245
Lubricity, corrected wear scar diameter (wsd 1,4) at 60 °C		μm	max.	520	520	520	520[g]	ISO 12156-1

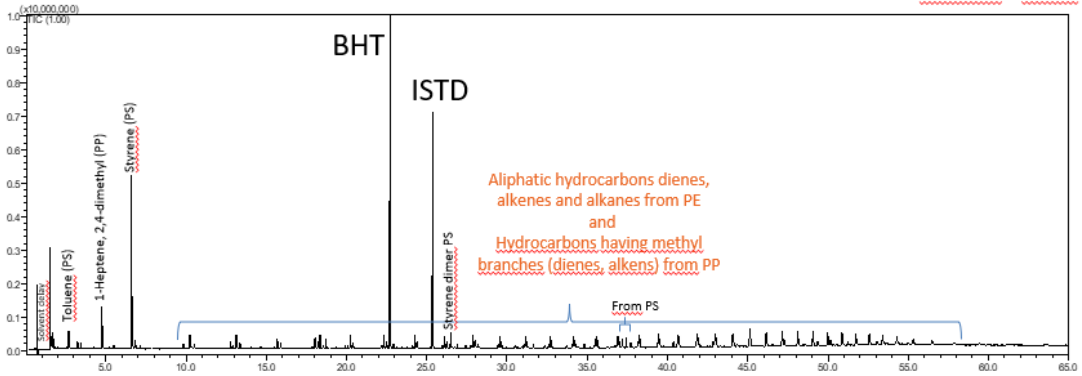
*(44)

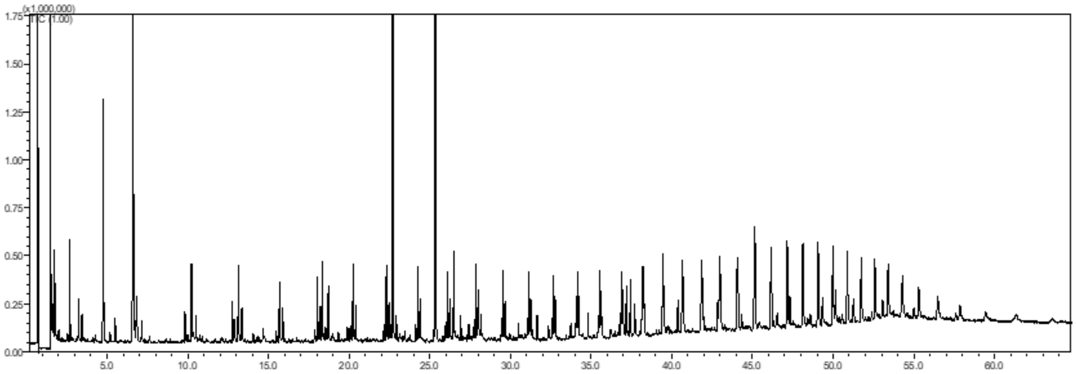
Appendix 4. Results from cold fluidization test.



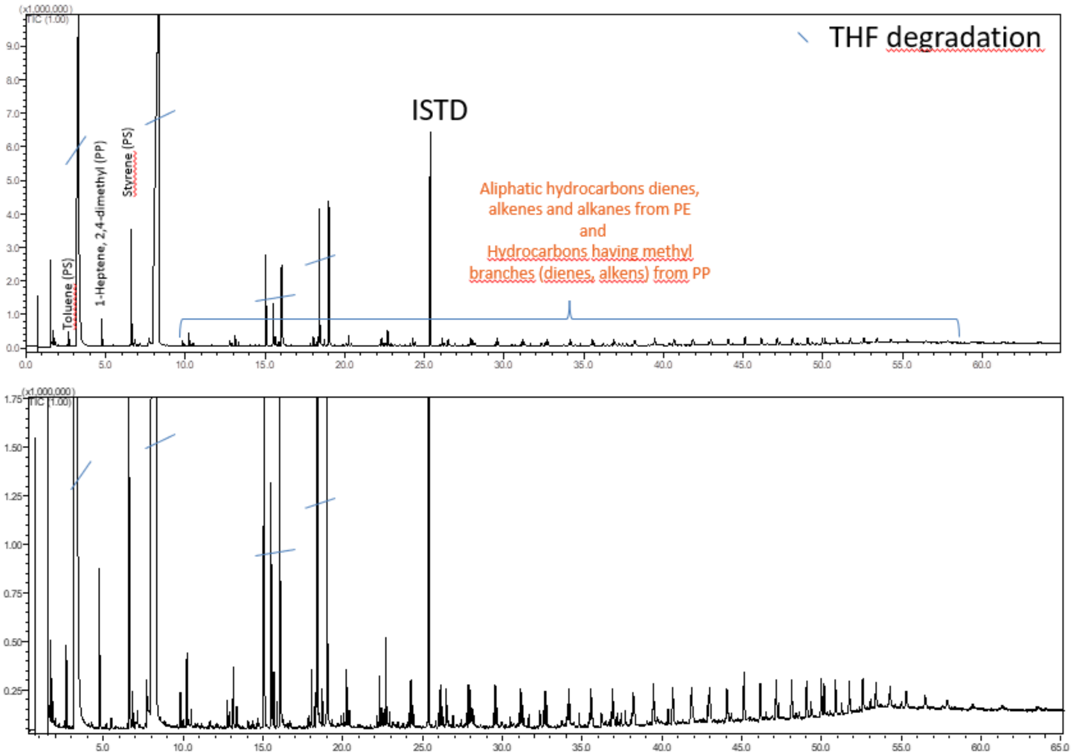
Appendix 5. GC/MS analysis results.

Thermal, T=500

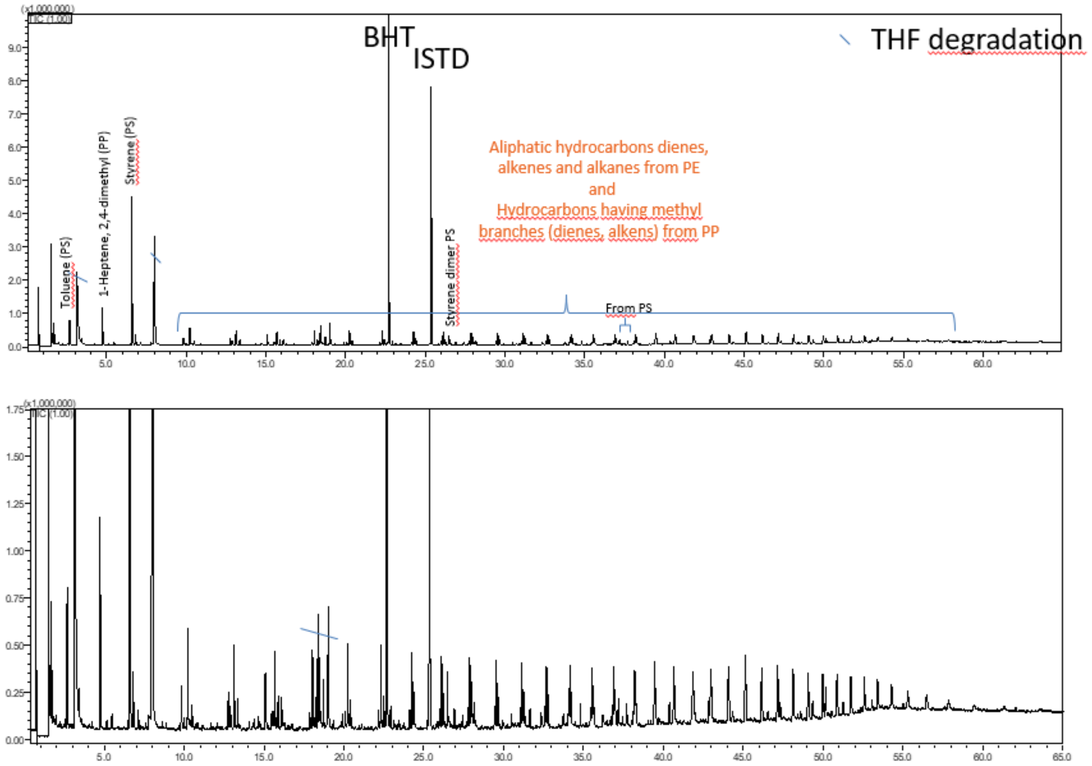


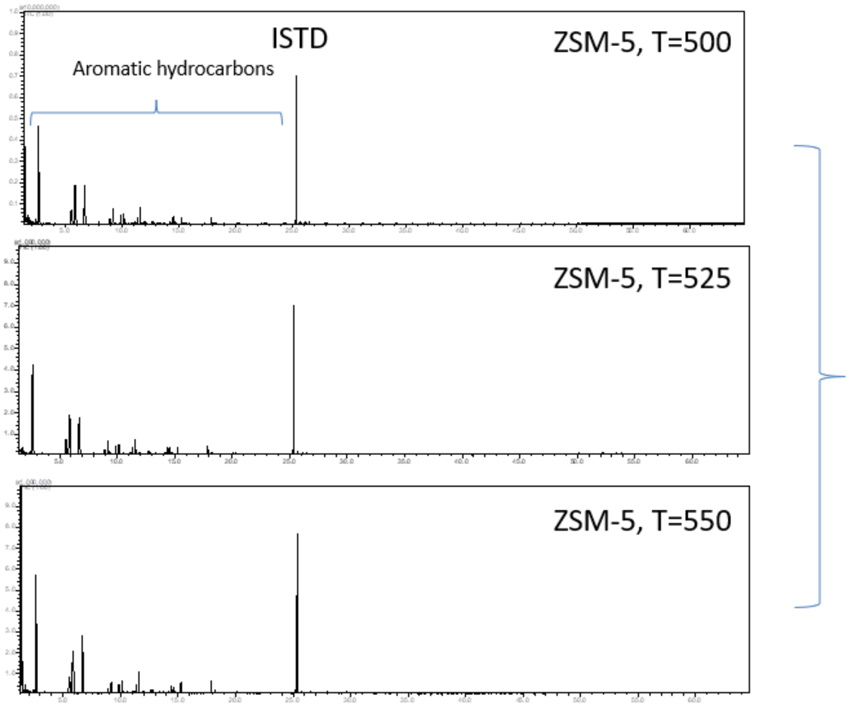


Thermal, T=525



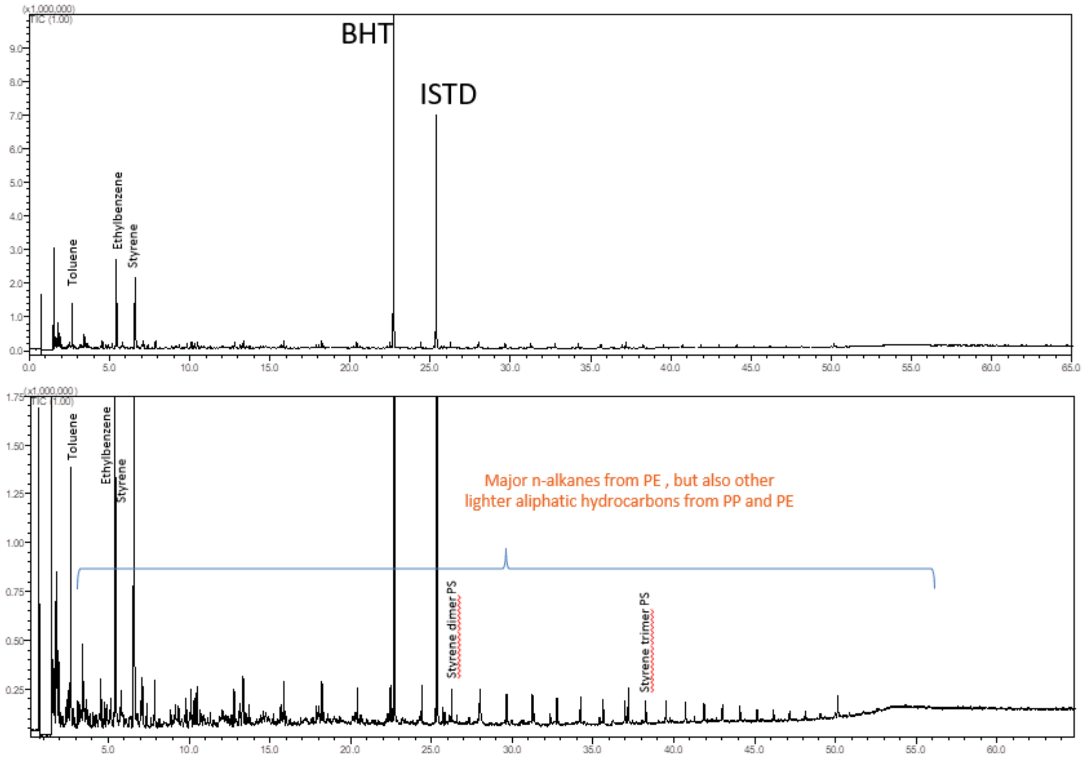
Thermal, T=550





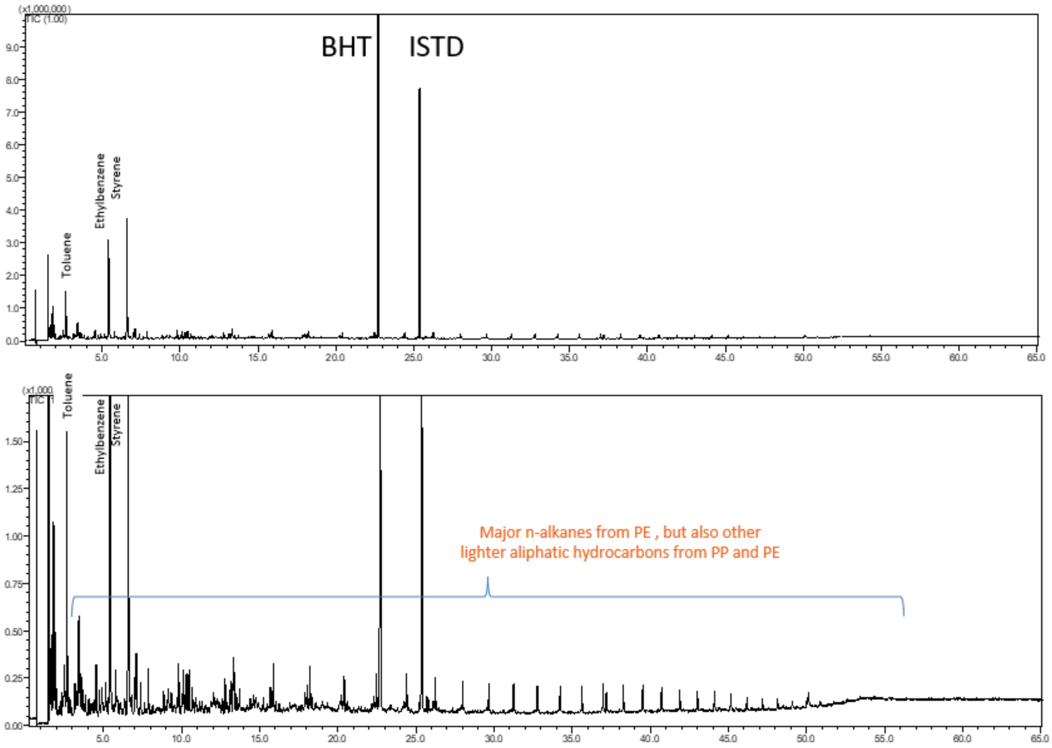
Quantified by Terva-method

Montmorillonite, T=500

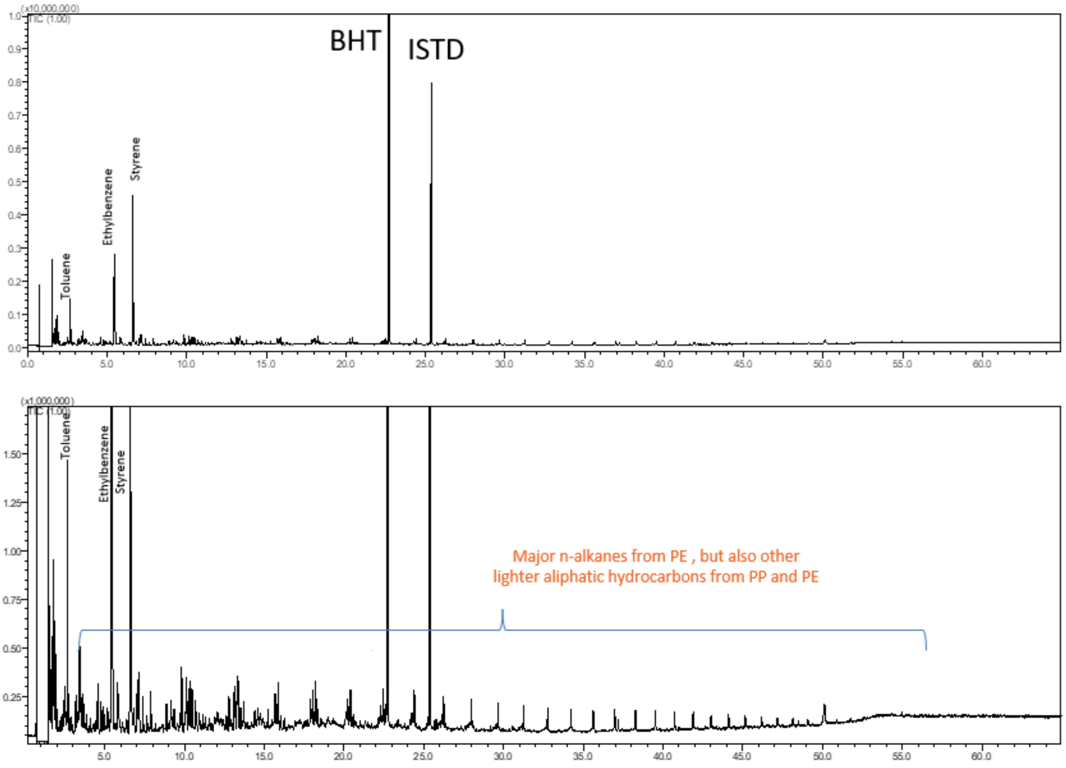


Major n-alkanes from PE , but also other lighter aliphatic hydrocarbons from PP and PE

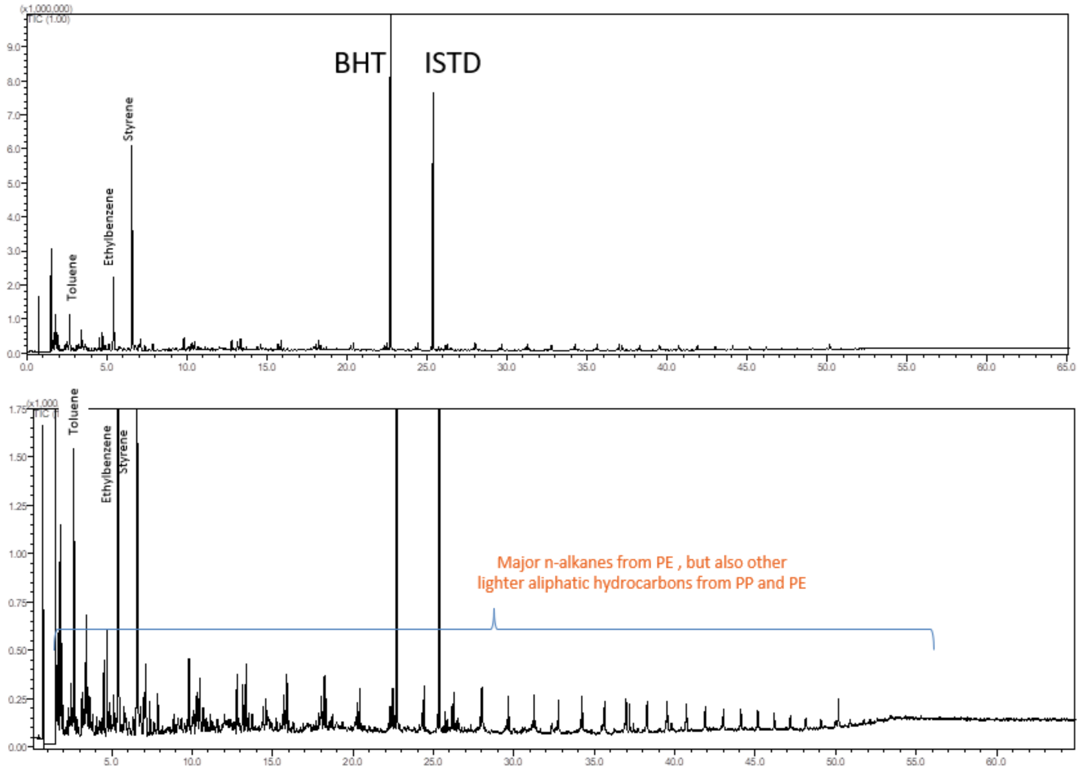
Montmorillonite, T=525



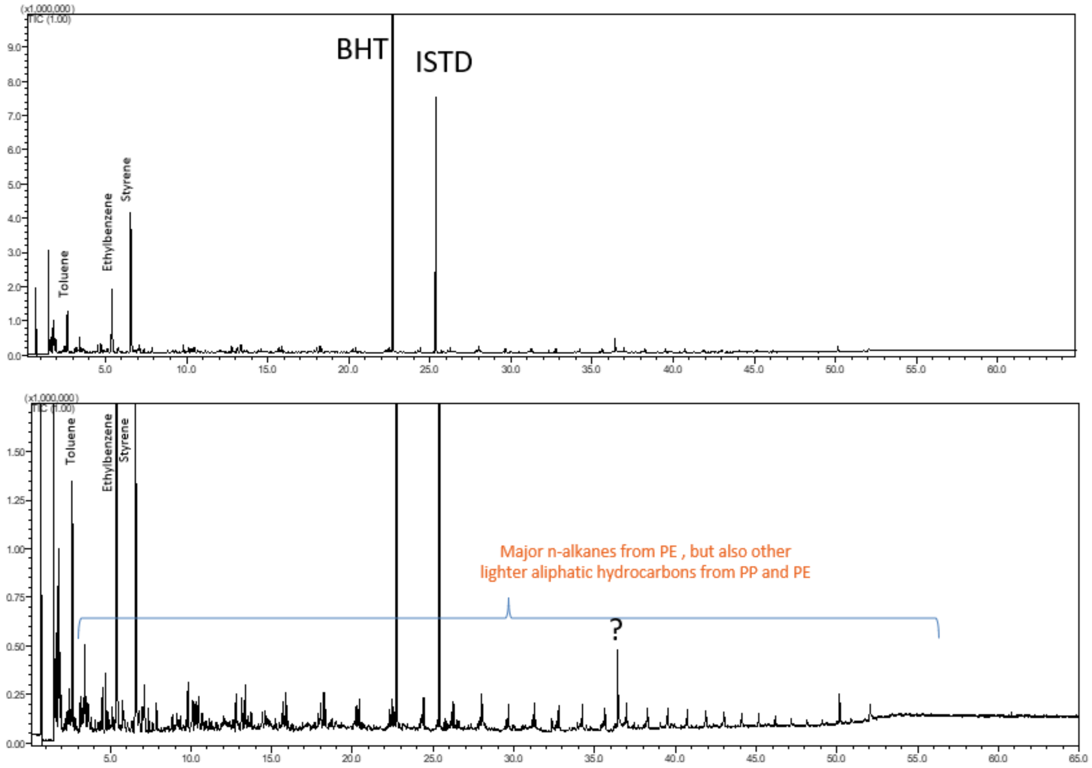
Montmorillonite, T=550



γ-alumina, T=500



γ-alumina, T=525



γ-alumina, T=550