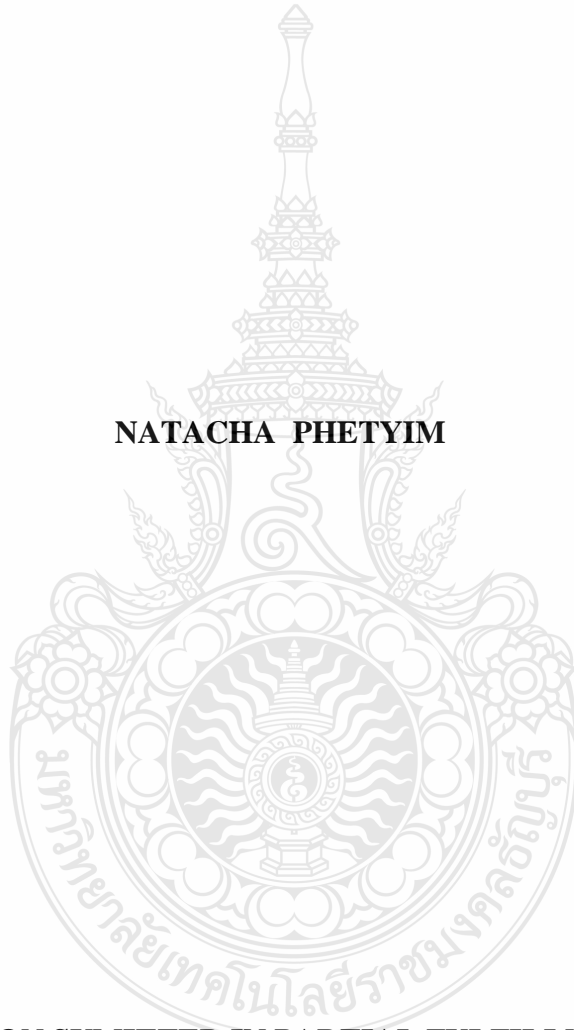


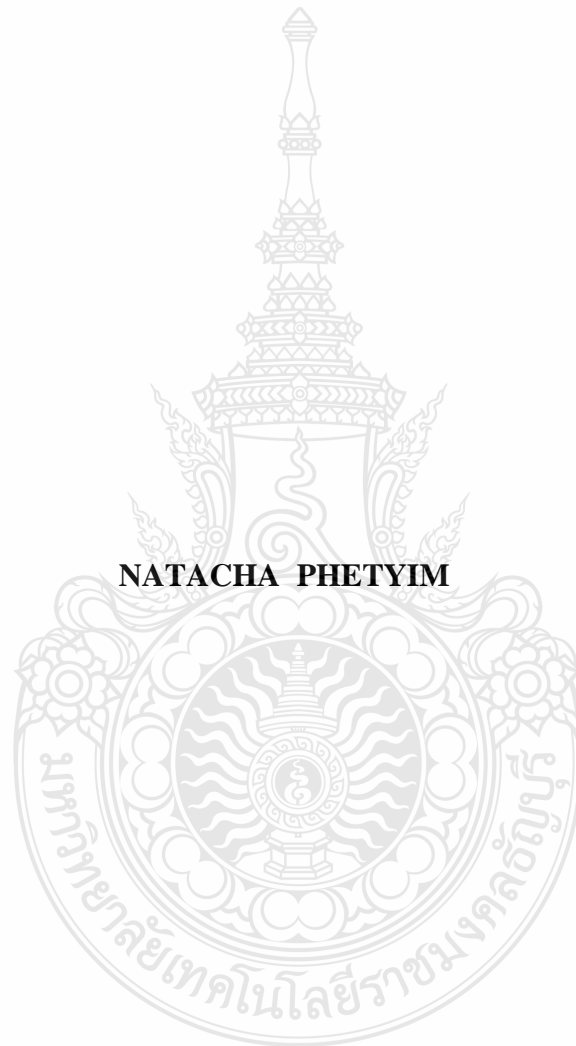
**PRODUCTION OF DIESEL-LIKE OIL FROM CO-PYROLYSIS BETWEEN  
USED LUBRICANT OIL AND PLASTIC WASTES**

**NATACHA PHETYIM**



**A DISSERTATION SUMMITTED IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF ENGINEERING  
PROGRAM IN ENERGY AND MATERIALS ENGINEERING  
(INTERNATIONAL PROGRAM)  
FACULTY OF ENGINEERING  
RAJAMANGALA UNIVERSITY OF TECHNOLOGY THANYABURI  
ACADEMIC YEAR 2018  
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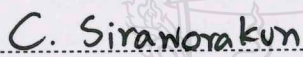
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**Program** Energy and Materials Engineering  
**Dissertation Advisor** Assistant Professor Sommai Pivsa-Art, Ph.D.  
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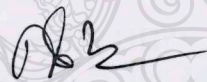
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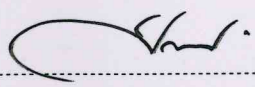
  
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Doctor of Engineering

  
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(Assistant Professor Sivakorn Anghong, Ph.D.)

January 11, 2019

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|-----------------------------|---|
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### ABSTRACT

Pyrolysis is the most effective method to recover hydrocarbon materials from plastic wastes. This study improved the pyrolysis process of solid plastic wastes. The co-pyrolysis process of used lubricant oils and mixed plastic wastes was developed. The optimization of co-pyrolysis conditions was studied to produce diesel-like oil product.

Plastic wastes included high-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS). The best proportions of raw materials in a laboratory scale were at atmospheric pressure at a final temperature of 450 °C with and without a catalyst. The investigated ratios between used lubricant oil (Oil) and plastic waste (Oil:HDPE:PP:PS) were 50:30:20:0, 50:30:0:20, 50:0:30:20, and 50:30:10:10 by weight. Kinetic of co-pyrolysis studied was Oil:HDPE, Oil:PP, and Oil:PS at heating rates of 5°C/min, 10°C/min, and 20°C/min. The appropriate proportion of raw materials was selected for co-pyrolysis prototype (10 kg/day).

It was found that oil produced from Oil:HDPE:PP:PS at the weight ratio of 50:30:20:0 gave standard diesel oil as specified by the Ministry of Energy (Thailand), except its lower standard of flash point. This proportion was tested with the co-pyrolysis prototype by studying oil property of three reactor temperature ranges (less than 400 °C, 400–425 °C, and 425–450 °C). The analysis of oil produced at 400–425 °C exhibited diesel-like fuel property. The parameters and activation energy data from the kinetic study of co-pyrolysis were used to design heat capacity of co-pyrolysis reaction. The co-pyrolysis prototype can be used to produce diesel-like fuel.

**Keywords:** co-pyrolysis, used lubricant oil, plastic wastes, prototype

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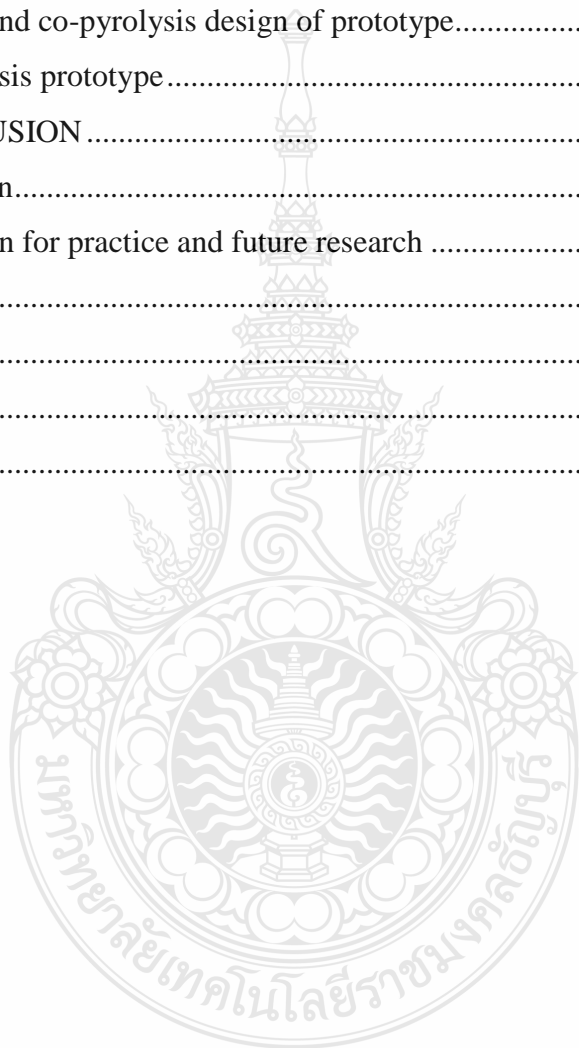


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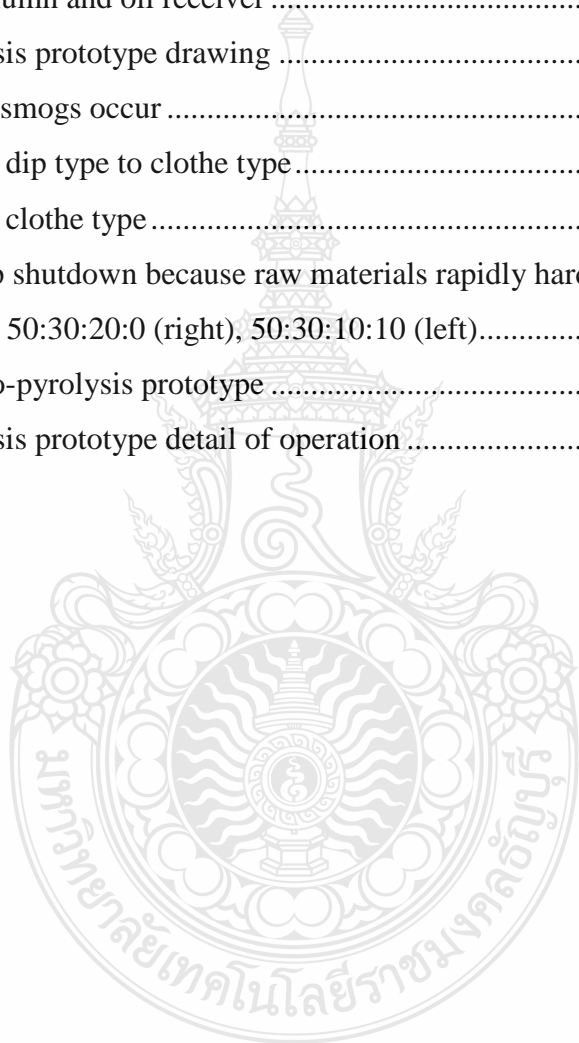
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## List of Abbreviations

|      |                              |
|------|------------------------------|
| HDPE | High density of polyethylene |
| Oil  | Waste lubricant oil          |
| PP   | Polypropylene                |
| PS   | Polystyrene                  |
| X    | Conversion                   |
| E    | Activation energy            |
| A    | pre-experiential factor      |



## CHAPTER 1 INTRODUCTION

### 1.1 Background and statement of the problems

The Pollution Control Department of the Ministry of Natural Resources and Environment of Thailand reported that solid waste and hazardous waste management is estimated to total 28 million tons of accumulated residual waste throughout the country and increase to 30 million tons after the implementation of the roadmap for a period of time. At the end of 2014, waste management can be combined. 13.2 million tons, and in the first six months of 2015 (January-June), the management has increased to 15 million tons, accounting for 50 percent of the total accumulated residual waste. The operations in the 6 urgent provinces are Phra Nakhon Si Ayutthaya, Saraburi, Lop Buri, Nakhon Pathom, Samut Prakan and Pathum Thani. The total amount of 11.04 million tons can be handled, 9.22 million tons, and 71 provinces, 18.96 million tons. They can be eliminated 5.78 million tons [1].

By recovering hydrocarbon materials, Pyrolysis is once a method to produce feedstock of petrochemical, gases, and oil fuel. Three types of MSW: (1) combustibles such as paper, wood, and organic waste; (2) non-combustibles such as metal, glass, and ceramic; and (3) plastics wastes. The major components plastic wastes such as high-density polyethylene (HDPE), low density polyethylene (LDPE), and liner low density polyethylene (LLDPE), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC), respectively.

In Thailand, hazardous waste from the community means waste products that are contaminated or contain substances that contain properties as toxic substances, flammable substances, oxidizing agents, peroxides, irritant substances, corrosive substances, easily reactive substances, explosive substance, substances that cause genetic changes, substances or other things that may cause harm to individuals, animals, plants or the environment which is caused by various activities within the residence Government offices, educational institutions, establishments including other places in the community. Most hazardous waste is used lubricants, car batteries and fluorescent lamps. For plastics containing pyrolysis, hazardous waste must be separated. However, used lubricants with high amounts of long paraffin and heavy metals can be degraded by heat into small hydrocarbons. During the pyrolysis reaction of mixed plastics, PE and PP are converted into a mixture of paraffin and olefins while PS is converted to aromatic monomer, dimmer and cutter. [2] Therefore, the mixture of plastic waste consisting of PE, PP, and PS and used lubricants can pass through the pyrolysis process to produce oil and chemical raw materials of hydrocarbons.

The waste used in the pyrolysis process, including automotive engine oil, brake fluid, transmission oil and power steering oil Due to the increasing number of cars, the amount of lubricant used in automotive engines increases every year. The recycling of used lubricant oil into fuel oil or lubricant oil could be a suitable option in reducing the environmental damage from hazardous waste as the oil waste contains high concentrations of heavy metals, varnishes, gums, and asphaltic compounds [3].

More than 80% of the used lubricants contain paraffin hydrocarbons containing carbon atoms between C<sub>26</sub>-C<sub>36</sub> [4] Bhaskar *et al.* reported the results of pyrolysis catalysts to waste lubricants with silica- Alumina - and iron oxide catalysts that support alumina at temperatures

of 400 ° C and under atmospheric pressure [5] Fe / SiO<sub>2</sub> catalysts reduce sulfur from 1640 to 90 ppm and produce hydrocarbons before the low molecular weight by cracking hydrocarbons with high molecular weight. Lam *et al.* studied waste oil using a microwave-induced pyrolysis process [6]. The results shown that both fresh and waste engine oil were composed mainly of linear and branched paraffin (>85%). By using the co-pyrolysis techniques, we can converse the long-chain hydrocarbons from plastic waste into more valuable compounds.

The waste plastic pyrolysis has low heat transfer and high viscosity of the melt polymer when the lubricant is mixed with plastic waste. It can act as a solvent to reduce viscosity and improve heat transfer in reactor of homogenous phase and it can reduce the activation energy in the form of co-feedstock [7]. Excellent reactor design is needed to ensure both high heat transfer rates for fast heating of polymers and reliable temperature control. There are operational problems due to the toughness of the melted plastic [8]. Optimization of conversion parameters such as catalyst selection, reactor design, temperature, pyrolysis and plastic ratio to catalysts play an important role in efficiently processing gasoline and diesel grades. [9]. Serrano *et al.* studied thermal cracking using a kiln reactor in two temperature zones (450 and 500° C for the first and second zones respectively) [10] and polyethylene raw materials. Low density and lubricant mixture used 60, 50:50, 60:40 and 70:30 (% wt.) Then fed into the reactor. All experiments have been converted to near completion (about 90%) with carbon atoms C<sub>1</sub>-C<sub>40</sub> hydrocarbons. Waste lubricants in the production of polyolefins increased in the form of liquid yields. But also improve the properties of oil products with a greater amount of paraffin than in the results of pyrolysis oil, rather than individual waste polyolefin products. However, the proportion of lubricants used in oil mixed with plastic waste cannot be more than 50% by weight of raw materials because higher oil content tends to produce oil products that are not like diesel [12,13]. Bartocci *et al.* [14] studies the pyrolysis of glycerol additions in pellet fuels while mixing with sawdust; for tablets with high glycerol content, the percentage of gas will increase. The proportion of composite materials tends to yield the ratio with the ingredients [15]. The previous study reported their study on co-pyrolysis individual and blended polyolefin (PE and PP) wastes and motor engine oil waste at 500 °C in a fixed bed reactor. The amount of waste lubricant oil in all proportions increased both of viscosity and specific gravity of liquid products [11]. thermal and catalytic cracking of a LDPE-lubricant oil base mixture in a continuous screw kiln reactor was investigated by [10] A significant proportion with increasing proportions of the lubricating oil base in the mixture shown increased selectivity of oil product in range of C<sub>13</sub>-C<sub>22</sub> and C<sub>23</sub>-C<sub>40</sub>. Miskolczi and Ateş [16] investigated the co-pyrolysis of real municipal plastic waste (MPW) and MPW derived heavy oil (HO) mixtures in the stirred reactor by 750 g of raw materials and 500 °C as a final temperature. The results shown increased of proportion of heavy oil can increased pyrolysis oil yield. Breyer *et al.* [15] studied the co-pyrolysis lab-scale experiments that were in a 5 litres batch reactor with a spiral stirrer. Raw materials were the mass of mixture between plastic waste from landfill and used oil and motor oil 412 and 574 g for each experiment. co-pyrolysis of plastic and oil mixture used 8 MJ to transferred to oil product. Kim *et al.* [17] report the kinetic parameters of pyrolysis mixing between waste car lubricants (WALO) and PS. Pyrolysis reactions are used in a 1 litter stirred reactor with mass 300 g specimens for every experiment, the temperature controls the temperature of the pyrolysis in the range of 300–500 ° C. Energy activation of co-pyrolysis is less than each type of raw material. Previous work mainly focused on the use of stirred reactors for joint pyrolysis of used lubricants and

plastic waste because this process is a simple design, low construction costs and lubricants oil used to increase heat transfer in the reactor.

This research aims to apply a two-stage methodology (melting and thermal cracking) for a prototype co-pyrolysis process for used lubricant oil blended with mixed waste plastics (HDPE, PP, and PS). The best proportion of raw material was determined at the laboratory scale and then studied kinetic parameter of co-pyrolysis (Oil/HDPE, Oil/PP, Oil/PS) by Thermogravimetric analysis technique to find activation energy and to design the heat capacity of co-pyrolysis reactions. The prototype scale of the optimised proportion from laboratory was selected to optimize the diesel-like oil products.

## **1.2 Purpose of this study**

- 1.2.1 To study co-pyrolysis process of used lubricant oil and mixed plastic wastes
  - 1.2.2 To optimize the co-pyrolysis conditions to produce diesel oil product
  - 1.2.3 To study the kinetic of co-pyrolysis of used lubricant oil and plastic wastes
- Scale up of the co-pyrolysis process

## **1.3 Scope of this study**

- 1.3.1 Study on co-pyrolysis of used lubricant oil and mixed plastic wastes: HDPE,PP and PS (batch reactor)
  - 1.3.2 Effect of catalyst on co-pyrolysis process
  - 1.3.2 Scale up of co-pyrolysis using a semi-batch reactor for pilot scale
- Oil product characterization

## **1.4 Benefit of this study**

- 1.4.1 Identify significant proportion of co-pyrolysis of used lubricant oil and mixed plastic wastes to produce diesel oil.
- 1.4.2 Design of co-pyrolysis prototype for industrial application
- 1.4.3 Recycle of hazardous and plastic wastes: high environmental impact

## **CHAPTER 2**

### **REVIEW OF THE LITERATURE**

#### **2.1 Feedstock recycling**

Pyrolysis is a process of chemical and thermal cracking of hydrocarbon materials, generally to provide smaller molecules by damage carbon-carbon bond. Probably can called, in the term thermolysis is more appropriate than pyrolysis, under absence or partial oxygen in atmospheric, low or high pressure system. However, excluded air is the reason for combustible protection, characteristic of products, product yield, and safety.

Pyrolysis can be operated at various temperature, heating rate, reaction time, pressure, and in the with and without catalysts. Waste plastic pyrolysis proceeds in three temperature range at low temperature (<400°C), medium temperature (400-600 °C) or high temperature (>600 °C). Generally, pyrolysis pressure are atmospheric, high pressure or vacuum pressure.

Thermal decomposition of polymers causes liquid, gas and solid residues in varying relative quantities. These liquids can be used as petrochemical and monomer fuels. Depending on the type of polymer or polymer mixture, operating conditions and type of reactor. As a rule, liquid and gas products are a mixture of different hydrocarbons. The problem of upgrading to be a commercial compound, such as gasoline, diesel oil or chemicals with added value by separating unwanted impurities, must be examined on a case-by-case basis. Solid wastes or ointments can combine filters, color and ash

Pyrolysis processes are endothermic reaction by breaking bond, so that supply enough of heat to the decomposed material is essential and generally rate-determining. Partial oxidation supplies such heat internally; the pyrolysis products are reacted by oxygen then combustion products can be occurred.

#### **2.2 Thermal analysis**

The thermal specification techniques of polymer such as:

- Differential scanning calorimetry (DSC), for specific heat measurement and phase change
- Differential thermal analysis (DTA), measuring temperature differences between samples and reference data and identifying occurrences and thermal effects and sudden changes in heat capacity
- Thermogravimetric analysis (TGA), for the assessment of thermal stability and decomposition temperature
- Thermomechanical analysis (TMA), for the mechanical response of the polymer system to temperature changes



- Flammability testing. Plastics used in furniture, mattresses, cars, electronic equipment, etc. must meet the requirements for fire and flame retardant behavior.

### 2.3 Major operating conditions

Important factors that influence the distribution of plastic pyrolysis products are summarized in Table 2.1.

**Table 2.1** Factors affecting product distribution

| <b>Factor of influence</b>                                   | <b>Effect</b>   |
|--|---|
| Chemical composition of the resins                           | The main pyrolysis products relate directly to the chemical structure and composition of the resin and its decomposition mechanisms. (purely heat or catalytic)                                     |
| Pyrolysis temperature and heating rate                       | Higher operating temperatures and high heat rates help increase fracture and help produce small molecules.  |
| Pyrolysis time   | Longer housing time allows for the second change of the main product to produce more, coke, tar and products with high heat, thus gradually obscuring the effect of traditional polymer structures. |
| Reactor type   | Mainly determined the quality of heat transfer, mixing time, housing, gas and liquid and the escape of the main product.  |
| Operating pressure   | Low pressure reduces condensation of the reaction parts which are coke and heavy.   |
| Presence of reactive gases, such as (air) oxygen or hydrogen | Such internal presence creates heat, dilutes the product and influences the balance of kinetics and mechanisms.   |
| Use of catalysis   | Their use influences the kinetics and mechanisms and hence the distribution of products.  |
| Additives incorporated                                       | General additives will evaporate or decompose. Some people may have influence on kinetics and mechanisms.   |
| Liquid or gas phase  | The pyrolysis of the liquid will delay the escape of the developing product.  |

## 2.4 Decomposition mode

As the pyrolysis role of plastics, it follows a complex path that cannot be explained by at least one chemical reaction. But only and still quite incomplete with empirical formulas with fractional coefficients stoichiometric or a comprehensive system of initial reactions. Moreover, the composition and structure of these reacting systems may vary according to the details of the molecular structure, such as chain abnormalities, initiator integration or catalysts, etc. The precise mechanism is of interest to science only. Considerations such as thermal effects and product distribution resulting under specific reaction conditions

The decomposition mode is often broken down according to the reaction pattern that is mainly determined by the molecular structure and the presence of the catalyst:

- The decomposition is a monomer unit (PMMA, PA 6). Most often it is called the zipper loosening. This decomposition mode is very interesting in practice because the monomer is a high value product, generally ordered to cost as much as many fuel costs.
- Random distribution of the main polymer chain (PE, PP) is a subset of the medium-length variable. The size distribution of the resulting parts is mostly Gaussian, with the average M.W. rising and rising when the temperature and time of the pyrolysis increases. Therefore, polyolefins will be transformed into waxes and PE oils, which often contain high olefins and sulfur-free diesel fuel. On the other hand, PP products provide more branched products.
- Both conventional decomposition (PS, PIB) in PS polystyrene plants can be easily converted to monomers due to the facility for pyrolysis product separation. For (Styrene and oligomer, ethylbenzene, toluene, benzene, etc.) However, in general, PS's large-scale production plants will not generate enough revenue. Scraps to feed pyrolysis units, even small industrial sizes
- Easy and stable molecular removal from adjacent atoms (PVC gives HCl effect, PVAc gives acetic acid, PVOH to water). The heat breakage causes unsaturated charring and residues in Chain loop
- Side chain removal followed by cross-linking and creating a porous residue that is stumped as well as non-volatile additives. This outline is followed by most thermosets and other linked polymers.

Polymer resins and their major possible products are collected in Table 2.2

**Table 2.2** Polymer resins and major possible products of thermal decomposition

| Resin | Mode of thermal decomposition | Low-temperature products | High-temperature products |
|-------|-------------------------------|--------------------------|---------------------------|
|-------|-------------------------------|--------------------------|---------------------------|

|      |  |   |                                      |
|------|--|---|--------------------------------------|
| PE   | Random chain rupture   | Waxes, paraffin oils, $\alpha$ -olefins | Gases and light oils                 |
| PP   | Random chain rupture   | Vaseline, olefins                       | Gases and light oils                 |
| PVC  | Elimination of HCl from the chain, chain dehydrogenation and cyclization | HCl (<300°C), benzene                   | Toluene (>300°C)                     |
| PS   | Combination of unzipping, and chain rupture, forming oligomers           | Styrene and its oligomers               | Styrene and its oligomers            |
| PMMA | Unzipping  | MMA                                     | Less MMA, more decomposition         |
| PTFE | Unzipping  | Monomer                                 | TFE                                  |
| PET  | $\beta$ -Hydrogen rearrangement and carboxylation                        | transfer, and de-vinyl terephthalate    | Benzoic acid and vinyl terephthalate |
| PA-6 | Unzipping  | Caprolactam                             |                                      |

## 2.5 Reactor type

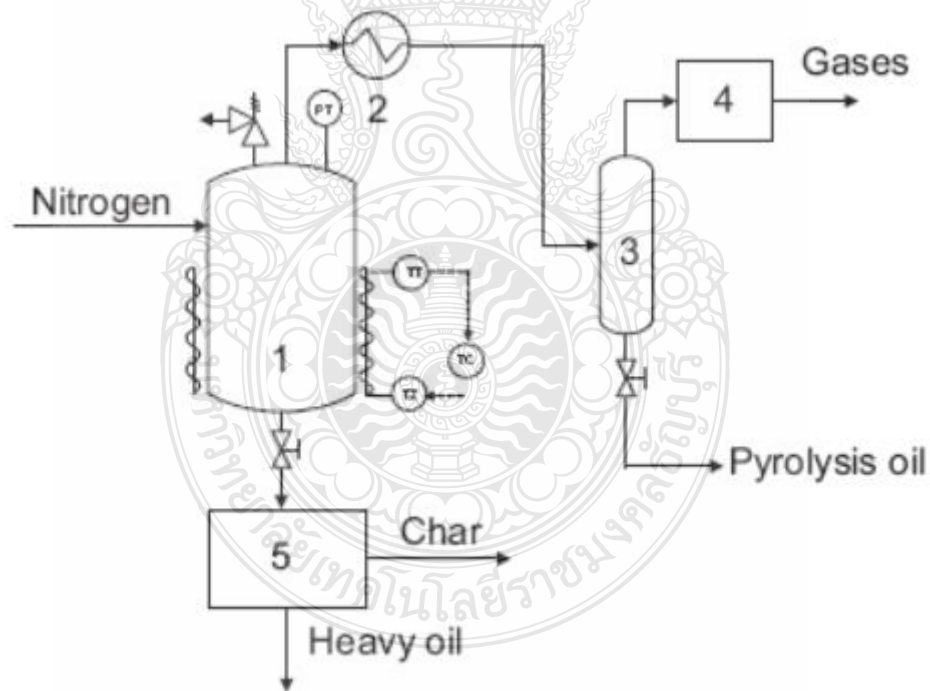
The type of reactor has a significant impact on the mixing of plastics and catalysts, housing time, heat transfer and reaction efficiency towards achieving the final desired product. Most pyrolysis plastics in the laboratory use a batch reactor such as a fluidized bed set, a bed reactor and a stirred tank reactor. The disadvantages of each reactor are as follows:

### 2.5.1 Batch and semi-batch reactor

The batch reactor is a closed system that does not have the inlet or outflow of the substrate or product while the high conversion reaction is made by leaving the substrate in the reactor which is one of its advantages. However, the disadvantage of batch reactors is the variability of products from different batches, high labor costs per batch and difficulty in controlling large production. The semi-batch reactor allows the addition of the substrate and the removal of the product at the same time, with the flexibility of adding the substrate over time as an additional advantage of the reaction selection in the semi-batch reactor. The disadvantage of the semi-reactor is similar to the labor cost model reactor. Most researchers want to use a batch reactor or a semi-batch reactor at a pyrolysis plastic laboratory level due to the simplest design and easy control of the working conditions. Normally pyrolysis in a batch or semi-batch reactor is made at a temperature range of 300–800 800C for thermal pyrolysis and catalysts. The drawback of this process

is the high tendency of coke formation on the surface of the catalyst, which will reduce the efficiency of the catalyst over time and cause a high solid residue in the process.

Sakata *et al.* [18] use a batch reactor to study the pyrolysis of PP and HDPE at 380 °C and 430 °C according to the use of various catalysts and without catalysts. The results showed that the liquid oil obtained from the catalytic catalyst was lower than the heat catalyst for some catalysts. The liquid yield from PP in the pyrolysis of heat is 80.1% wt. and from HDPE to 69.3% wt. by using many catalysts such as silica-alumina (SA-1) and HZSM-5. Both PP and HDPE decreased to 47–78% wt. and 49.8–67.8% by weight respectively. Therefore, different catalysts may have different reactions with plastic types. However, the trend of coke formation on the surface of the catalyst may be one of the reasons that the efficiency of the catalyst in the batch reactor is reduced. Abbas-Abadi *et al.* [19] studied the PP pyrolysis in a semi-batch reactor using the FCC catalyst at 450 °C. The results showed that the yield of the liquid was as high as 92.3%. And partly semi-partial, with a stirring machine that works at different speeds depending on the desired setting, as shown in Figure 2.1 Seo *et al.* [20] Study the pyrolysis of HDPE using a batch reactor with a stirrer at 450 °C. The stirring speed is 200 rpm. The liquid oil is higher than Sakata and the corps in Pyro. Anodic oxidation of approximately 84.0 percent by weight.

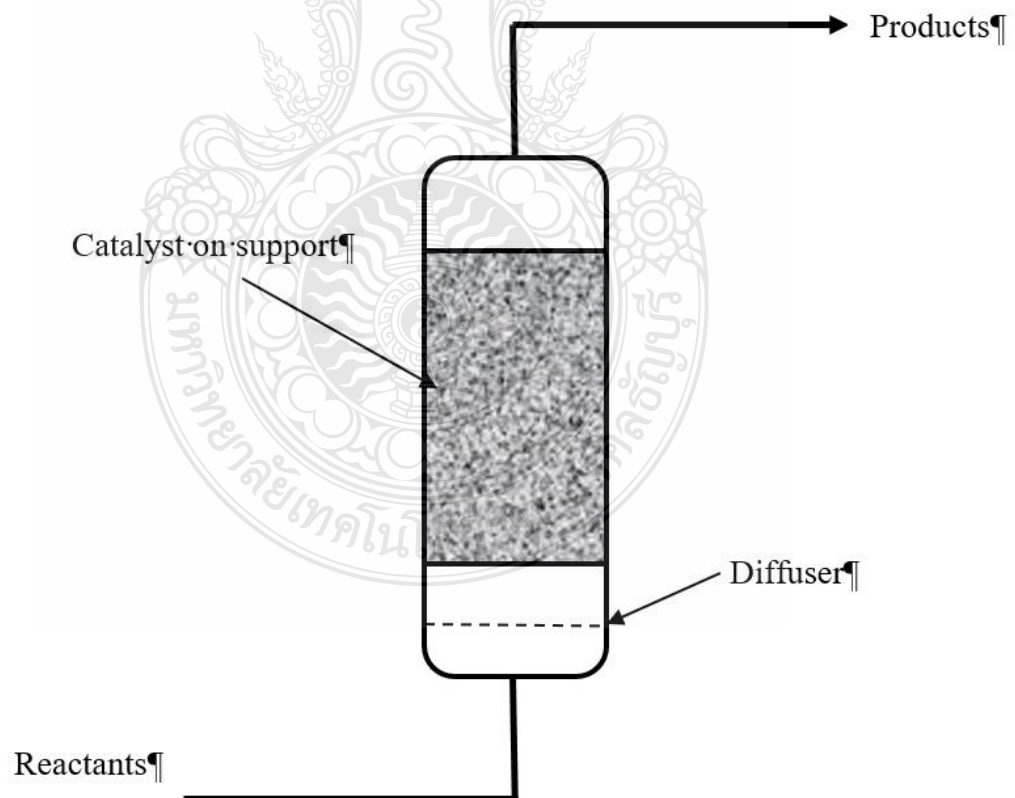


**Figure 2.1** Batch reactor with stirrer equipment. [16]

### 2.5.2. Packed and fluidized bed reactor

Packed-bed reactors often contain particles or catalysts in a fixed bed, as shown in Figure 2.2. It is easy to design, but there are some limitations, such as particle size and

irregular shape of the plastic as the material that will cause problems during the feeding process. In addition, the surface area of the catalyst that can be reached by the reaction is still limited. However, there are many researches on the use of a fixed bed reactor for pyrolysis plastics. The fixed bed reactor is only used as a pyrolysis secondary reactor because the main pyrolysis product can be easily fed into a fixed bed reactor which generally consists of liquid and gas phase. Onu *et al.* [21] use the fluoride gas through, and the particles are brought into the liquid state. Therefore, the catalyst has better access because the catalyst has a good mix with the occurrence. This will reduce the variability of process conditions with good heat transfer. In addition, it is more flexible than batch reactors because it can avoid frequent charging of raw materials and the process does not need to return to work often. Therefore, for the general design size, the fluidized bed reactor is the best reactor to be used in the prototype plant due to low operating costs. Therefore, the fluidized bed reactor concludes that it is the best reactor in the pyrolysis plastic reaction because the catalyst can be reused many times without the need for release come out. In addition, it is more flexible than a batch reactor because it can avoid charging the material frequently for continuous processes and the process does not need to return to work frequently. Therefore, the fluidized bed reactor is the most suitable reactor for large-scale applications in terms of economic perspective.



**Figure 2.2** Diagram of fixed-bed reactor.

## 2.6 Mechanism of thermal degradation [22]

The thermal decomposition mechanism of polymers is an interesting topic. But from the basic perspective of polymer reactions only but also understand the characteristics of heat resistance, polymer processes such as extrusion or injection molding. Thermal decomposition of polymers consists of two different reactions that occur simultaneously in the reactor. One is the random linking that causes molecular weight reduction of raw polymers and the other is the chain break of the C-C bond. The chain-end scission takes place at the gases-liquid interface in the working reactor [23]. The type and composition of the pyrolysis products give useful information about mechanism of thermal degradation [24].

Thermal decomposition of polymers followed by chain degradation (Also known as unzipping) (Eqs. (2.1 and 2.2)) or random degradation paths (Eq (2.3))

As shown below:



Chain deterioration begins from the end of the chain and releases the monomer unit continuously. This type of degradation path is also called reaction. de-polymerization Which relates to the release of monomer units continuously from the end of the chain. Such reactions are in contrast to the diffusion process of polymerization and occur through free radical mechanisms. The type of decomposition, the molecular weight of the polymer decreases slowly and releases a large amount of monomer at the same time. Random decay occurs at any random point throughout the polymer chain. This is a process that goes back to the polymer condensation process, in which polymers decompose to a lower molecular weight piece. For random decomposition that occurs, polymer chains do not need to be carried to any site. [25] PE also receives

Random decomposition by moving the hydrogen atom from one carbon to another, thus creating two pieces Polystyrene will decompose by chain extraction. Monomers obtained from these polymers are usually low and pyrolysis parts are larger than the corresponding monomer units. The method of thermal decomposition of polymers can be used in 3 methods.

### 2.6.1 Batch reactor method.

Thermal degradation of waste plastics can be performed in a glass reactor under the atmospheric pressure of the sample packed into the bottom of the reactor for thermal degradation Removal of the reactor containing nitrogen at a flow rate of 10 mL / min at 120 °C for 60 minutes will have to eliminate the water absorbed from the plastic sample. After stopping the flow of nitrogen, the temperature of the reactor will increase as the

decomposition temperature (430 °C) at the heat rate of 3 °C min<sup>-1</sup> and the plastic waste bed temperature is used as the decomposition temperature. Gas-condensed products (using condenser, cold water) with liquid products and stuck in the measuring jar quantitative analysis of liquid products can be done by using gas chromatography along with ion flame detectors, atomic emission detectors, ion chromatography detectors and machines. Mass selection detection solid waste can be identified by FTIR spectrometer. [26]

#### 2.6.2 Thermogravimetric analysis method.

Thermogravimetric analysis (TGA) can be used for inspection. Oxidation and thermal degradation of polymers [27] degradation rate in TGA ( $dX / dt$ ) means the rate of change of the conversion level The degree of degradation or conversion can be calculated in the form of mass as shown below:

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty} \quad (2.4)$$

where  $W_0$ ,  $W$  and  $W_\infty$  are the initial weight, the actual weight at each point of the curve and the final weight measured at the end of the degradation process, respectively [28] in TGA.

Sample tools are sent to a constant heating rate from room temperature to 600 ° C under nitrogen flow. Reaction products can be analyzed by gas chromatography.

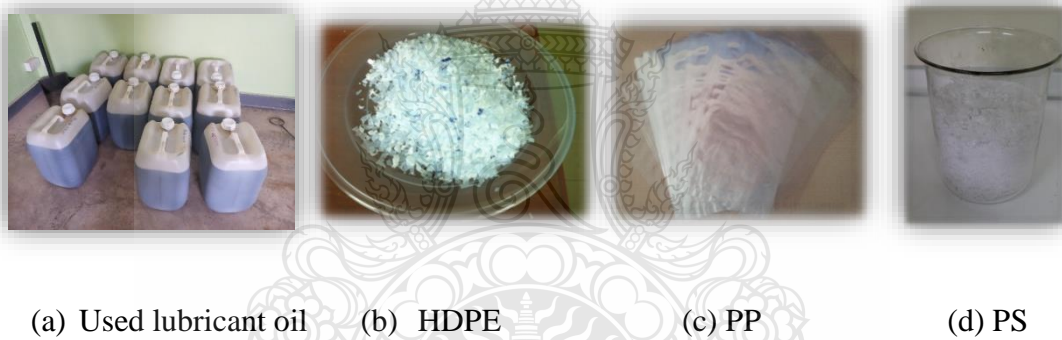
#### 2.6.3 Pyrolysis GC/MS method.

In this way, the evaporation pyrolysis products at different temperatures can specified with the help of GC / MS, pyrolysis uses a technique that disables small stainless steel cups filled with samples, being dumped into a small vertical kiln by independent gravity falling with a mechanism. Push button This system is designed to precisely control the temperature. When the system starts up, the controller will stop sampling after 0.5 minutes and the pyrolysis gas from the sample will be sent directly to the GC / MS analysis system. [29]

## CHAPTER 3 RESEARCH METHODOLOGY

### 3.1 Materials

The waste oil used in this research is API SN 0W20 from the Honda Center, Thanyaburi. Dehydration of waste lubricant oil is heated at 110 ° C for 1 hour by stirring at 200 rpm. For example, HDPE plastic waste is collected from sample drinking bottles, PP plastic waste collected from food bags and samples of PS plastic waste into containers. Food box packaging All plastic waste is crushed to a particle size of about 5-7 mm.



**Figure 3.1** Raw materials



**Figure 3.2** Zeolite (3A < 10µm powder)



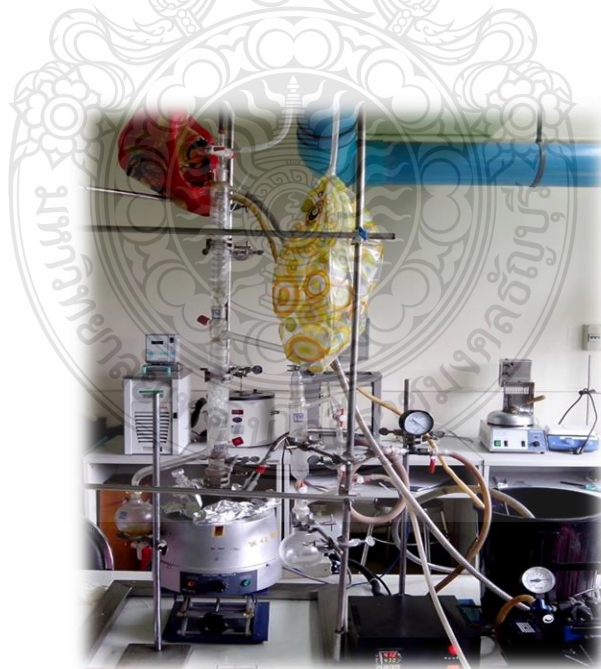
### 3.2 Decomposition analysis

Waste lubricant oil sample, HDPE, PP and PS were checked the temperature decomposition by temperature analysis (TGA) using NETZSCH TG 209 F3, about 10 mg of waste oil, PP and HDPE samples respectively, and 5 mg PS samples were heated to the temperature. Was kept for 10 minutes at a temperature (32 °C) and increased linearly from 32 °C to 700°C using a heat rate of 20 °C / min in nitrogen gas (N<sub>2</sub>) flow rate 20 ml / min [30]

### 3.3 Pyrolysis experiments

#### 3.3.1 Laboratory scale co-pyrolysis

The co-pyrolysis lab-scale experiments were carried out in the unstirred batch reactor. It consists of a 1-liter reactor in borosilicate glass with thermocouple and PID controller operated with atmospheric pressure of nitrogen. 350 g of raw materials and 0.5 wt.% of zeolite as catalyst were placed in the reactor in each experiment and then heated from room temperature to the final temperature as 450°C for 4 hours (at first drop of liquid come out).



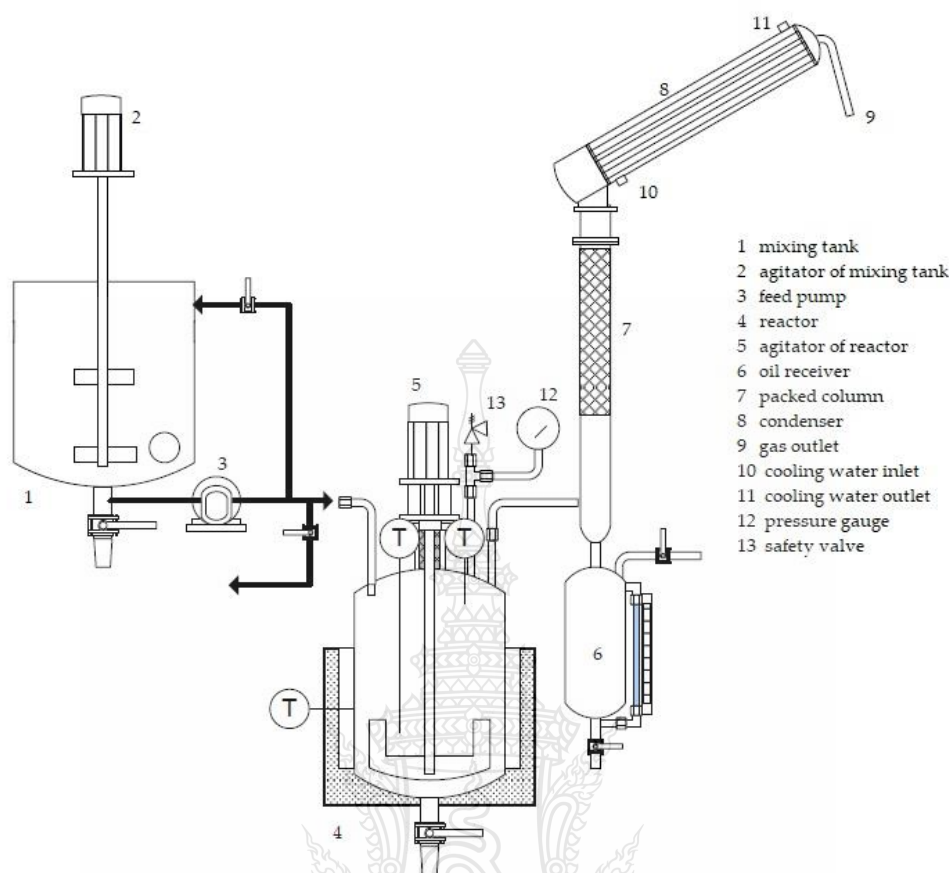
**Figure 3.3** Pyrolysis set up for lab- scale

### 3.3.2 Co-pyrolysis prototype

The co-pyrolysis prototype set up is shown in Fig. 3.4. Waste lubricant oil blended with HDPE, PP and PS with optimum proportion was selected from laboratory scale using final temperature 450 °C (inside reactor) without catalyst. Waste lubricant oil was placed in a mixing tank and heated to 180 °C and then plastic wastes consist of HDPE and PP were melted in homogenous phase (about 1 hour), and then feed into the stirred reactor and heated from room temperature be up to 300°C (10°C /min) under 0.5 bar nitrogen gas. The melting tank and reactor are made of 304 stainless steel and capacity of 15 L for reactor and 20 L respectively. The temperature inside reactor vessel at top and bottom were measured by thermocouple type k and the jacket temperature (heater) was controlled by PID controller. The Thermal cracking occurred inside the reactor, gases from the reactor is driven through the packed column and then the pyrolysis oil is condensed by cooling the water from the ice bath. (The cooling channel is about 15°C) Pyrolysis oil storage by the oil receiver at three reactors is 300-400°C, 400-425°C and 425-450°C. Uncondensed gases to release outside. Oil and solids calculated by weighting the yield of the gas calculated by removing the total amount of oil and solid output.

**Table 3.1** Specification of lab-scale and prototype

| <b>Specification</b> | <b>Lab-Scale</b> | <b>Prototype</b> |
|----------------------|------------------|------------------|
| Feed                 | Batch            | Semi-batch       |
| Reactor volume       | 1 liter          | 20 liter         |
| Heating rate         | not control      | 10 °C/min        |
| Pressure             | atmospheric      | 0.5 bar gauge    |
| Nitrogen flow        | Vacuum purge     | Sweep purge      |
| Cooling water        | Ice bath         | Ice bath         |
| Heater               | Heating mental   | Heating band     |
| Agitation            | Unstirred        | Stirred          |



**Figure 3.4** Diagram co-pyrolysis prototype for a 10 kg/day

### 3.4 Effect of feedstock proportion

#### 3.4.1 Each type of waste plastic

Pyrolysis of waste motor oil only, waste motor oil blend with each type of waste plastic; Oil:HDPE, Oil:PS, and Oil:PP were studied in proportions 100:0, 75:25, 60:40, 50:50, 40:60, 25:75, and 0:100 by weight. The accumulation of liquid products stopped and no longer found the gas products in the system. The reactor was visually inspected to ensure the reaction was complete. The yield of solid products is determined by measuring the weight changes in the reactor, the yield of liquid products is determined by measuring the weight gain in the collected vessel. The output of the gas product is determined by the balance of mass and assumes that the mass of the sample is not

proportional to the measurement of liquid and solid products from the system in the form of gases

#### 3.4.2 Three types of waste plastic

Co-pyrolysis of used lubricant oil mixed with two type of plastic waste were studied in proportions (Oil:HDPE:PP:PS) of 50:30:10:10, 40:50:5:5, and 20:60:10:10 percent by weight with and without catalyst. The reactor was controlled for 4 hours to ensure that the reaction was completed. The yield of oil product was determined by measurement of the weight of oil in the collected vessels under condenser and the yield of solid product was determined by measuring weight of residue after the end of reaction. The gaseous product yield was determined by mass balance and assumed that total amount of all products was equal to the initial raw materials.

#### 3.4.3 Two types of waste plastic

The study of co- pyrolysis of used lubricants mixed with two types of plastic waste in proportion (oil: HDPE: PP: PS) 50:30:20:0, 50:30:0:20, and 50:0:30:20 percent by weight without catalysts and fixed oil waste equal to 50 wt.% The reactor is controlled for 4 hours to ensure the reaction is complete. The production of oil products is determined by measuring the weight of the oil in the vessel collected under the condenser and the product yield of the solid product is determined by measuring the weight of the residue after the reaction ends. Gas yield is determined by mass balance and assumes that the total amount of the product is equal to the initial raw material.

### 3.5 Product characteristic

The properties of the oil samples were tested as ASTM follows: the flash point (ASTMD 93) was determined using a Pensky Martens model HFP 380 (Walter Herzog GmbH, Lauda-Königshofen, Germany); the viscosity @ 40 °C (ASTM D 445) using a viscometer bath model TV2500B (PM Tamson Instruments, Bleiswijk, Netherlands) and cannon viscometer glass; the color measurement (ASTM D 1500) using a model Comparator 3000 series (Lovibond, Dortmund, Germany); the specific gravity@60°F (ASTM D1298) using a glass hydrometer; and the distillation temperature@ 90%

recovery (ASTM D86) and cetane index (ASTM D 976) using an Automated Distillation Tester model AD-6 (TANAKA Scientific Limited, Tokyo, Japan). The pyrolysis oil flash point, specific gravity, distillation temperature at 90% recovery, cetane index (calculated from the density and temperature of distillation at 50% recovery), viscosity, and color were compared with standards for diesel oil specified by the Department of Energy Business, Ministry of Energy of Thailand. The chemical composition of the hydrocarbon compounds of the pyrolytic oils was analyzed using a gas chromatography and mass spectrometry analyzer (GC-MS, QP2010, Shimadzu, Kyoto, Japan) with an HP-5 column 30 m in length and 0.25 mm in diameter, a 10:1 split, a Helium gas flowrate of 0.9 mL/min, and an oven temperature of 170 °C to 320 °C [31]. Chemical composition of oil products from GC-MS were rearranged in grouping: four groups based on their structure (paraffin, olefin, cyclic and aromatic compounds). The number of carbon atoms were divided into three ranges: gasoline oil (C<sub>6</sub>-C<sub>12</sub>), diesel oil (C<sub>13</sub>-C<sub>19</sub>), and heavy oil (>C<sub>20</sub>).



**Figure 3.5** Distillation ASTM D 86 and cetane index ASTM 976



**Figure 3.6** Color ASTM D 1500



**Figure 3.7** Flash point ASTM D 93



**Figure 3.8** Viscosity ASTM D 445



**Figure 3.9** Specific gravity ASTM D 1298

### 3.6 Kinetic of co-pyrolysis [17]

The kinetic parameters of three components of co-pyrolysis (Oil:HDPE, Oil:PP Oil:PS at ratio 1:1) were investigated by TGA curve and data. X is conversion, calculated from different value of initial weight of materials and weight of materials at % weight losses (10% to 90%). The instantaneous rate of conversion,  $dX/dt$  is obtained from differential thermogravimetric analysis (DTG) at different proportion of raw materials between waste oil and each type of waste plastic types such as HDPE, PP, and PS at three different heating rate: 5 °C/min, 10 °C/min, and 20 °C/min. The differential method of thermogravimetric analysis was followed:

The rate of conversion,  $dX/dt$ , in thermal decomposition is expressed by

$$\frac{dx}{dt} = kf(x) \quad (3.1)$$

The reaction rate constant k is expressed by the Arrhenius equation

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (3.2)$$

A function of conversion independent of temperature,  $f(x)$ , is expressed as

$$f(x) = x^n \quad (3.3)$$

Substituting Eq. (4.2) and (4.3) into Eq. (4.1) and taking a natural logarithm, the above equation yields

$$\frac{dX}{dt} = A \exp\left(\frac{-E}{RT}\right) \quad (3.4)$$

$$\ln \frac{dX}{dt} = \ln A x^n \exp\left(\frac{-E}{RT}\right) \quad (3.5)$$

Rearrange

$$\ln \frac{dX}{dt} = \ln A X^n - \frac{E}{R} \frac{1}{T} \quad (3.6)$$

The activation of E energy according to Eq. (3.6) is determined by the relationship between  $\ln dX / dt$  and  $1 / T$ . Therefore, it has a family of parallel lines of slope  $(-E) / R$ . with the selected conversion (0.1-0.9). Interception at the y axis ( $\ln(AX^n)$ ) can be calculated from curve of  $\ln dx/dt$  and  $1/T$  in each conversion. The sequence of reactions

(n) and pre-experience factors (A) are derived from finding the curve according to Eq (3.7).

$$\ln(A \cdot X^n) = \ln A + n \ln(X) \quad (3.7)$$

Slope of curve is  $\frac{-E}{R}$ , Finding A were used  $R = 8.314 \text{ J/mol}\cdot\text{K}$

### 3.7 Prototype design of co-pyrolysis

Literature reviews were indicated the batch reactor should to be the main design as reactor because it is easy to operated and low cost of construction. Therefore, design concept of co-pyrolysis prototype as followed:

- Keep composition of raw materials constant.
- Reactor temperature can be reach 450°C.
- Heating rate and temperature pattern for controller of reactor temperature should be optimized.
- Materials were selected for maximum temperature of reactor (600°C)
- Maximum pressure inside the reactor was investigated for selected safety valve.
- Cooling water temperature was selected for design type of cooling bath.
- Temperature of melting tank was studied as homogenous phase.



## CHAPTER 4

### RESEARCH RESULT

#### 4.1 Thermal decomposition of raw materials

From Figure 4.1 to 4.4 presents the curve of thermogravimetric analysis (TGA) of each raw materials (used lubricant oil and waste plastics) that used in this research. Used lubricant oil decomposes at two steps: the first step occurs between temperature range 170°C and 290°C, while the second step occurs at nearly 400°C [12], while HDPE, PS and PP decompose temperature at 470-500°C, 410-440°C and 420-480°C, respectively. According to thermal stability of feedstock as follows: HDPE>PP>PS>used lubricant oil, confirm the TGA curve from [13]. The co-pyrolysis of used lubricant oil blend with mixed plastic (HDPE, PP, and PS) could be decomposed completely at 500°C. Due to the limitation of the heating mental equipment that used for pyrolysis in lab-scale, the final temperature of co-pyrolysis experiments was selected at 450°C. [31]

Properties of waste lubricant oil before co-pyrolysis was shown in table 4.1: viscosity@100 °C: 9.12 cSt; flash point: 194 °C; specific gravity: 0.878. The waste lubricant oil was dehydrated by heating at 110 °C for 1 h with stirring at 200 rpm before place in the pyrolysis reactor with waste plastics.

**Table 4.1** Properties of used lubricant oil

| viscosity (cSt) @ 100°C | Flash point (°C) | Specific gravity | color |
|-------------------------|------------------|------------------|-------|
| 9.12                    | 194              | 0.878            | >8    |

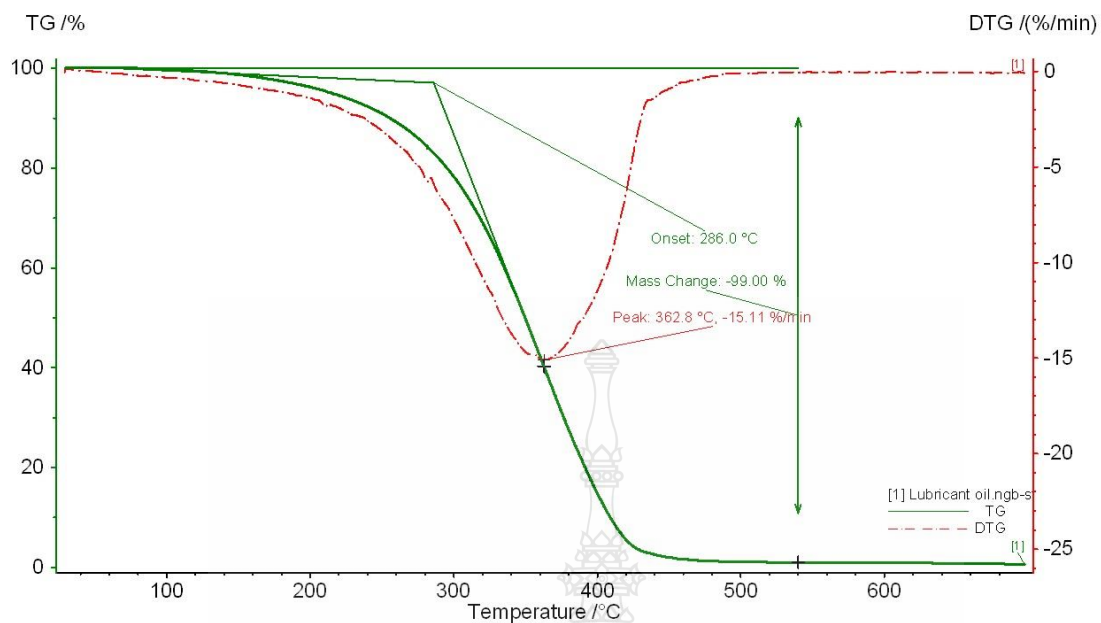


Figure 4.1 TGA curve of used lubricant oil

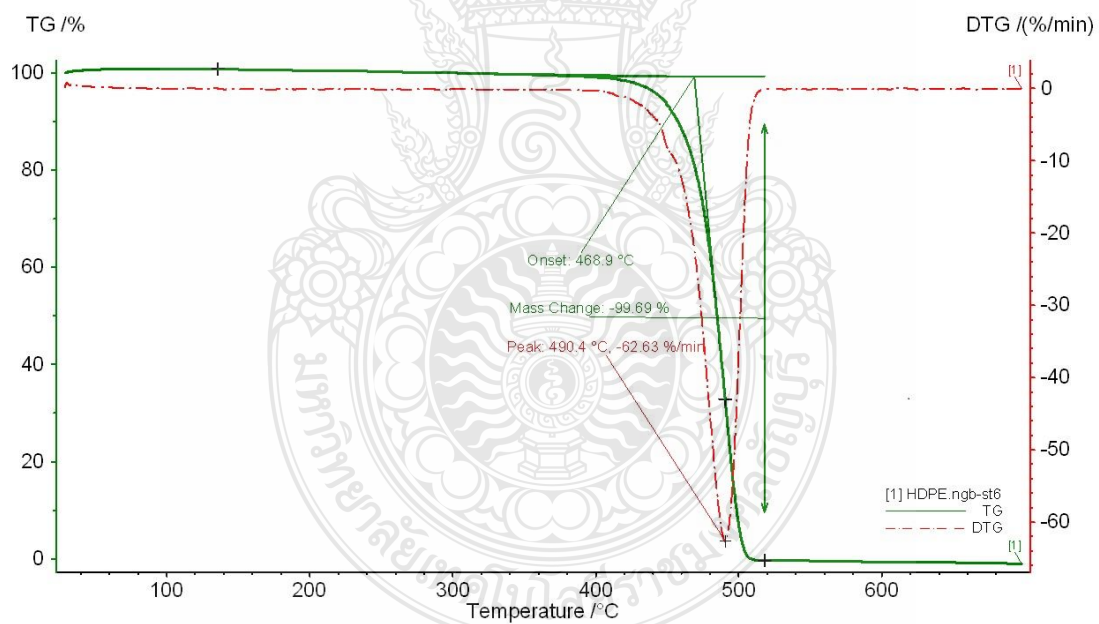
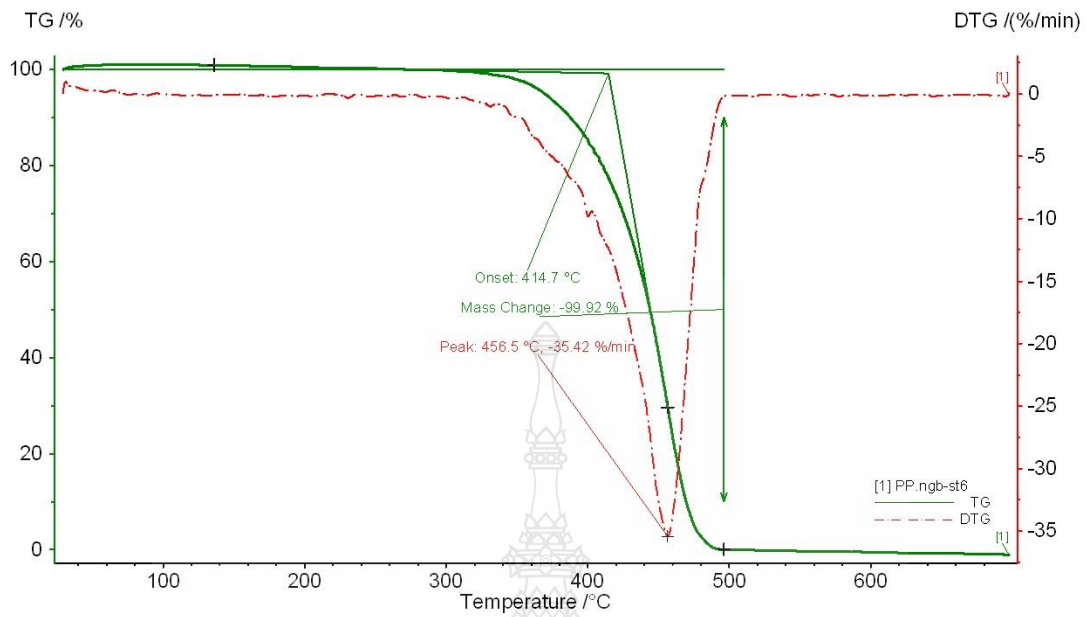
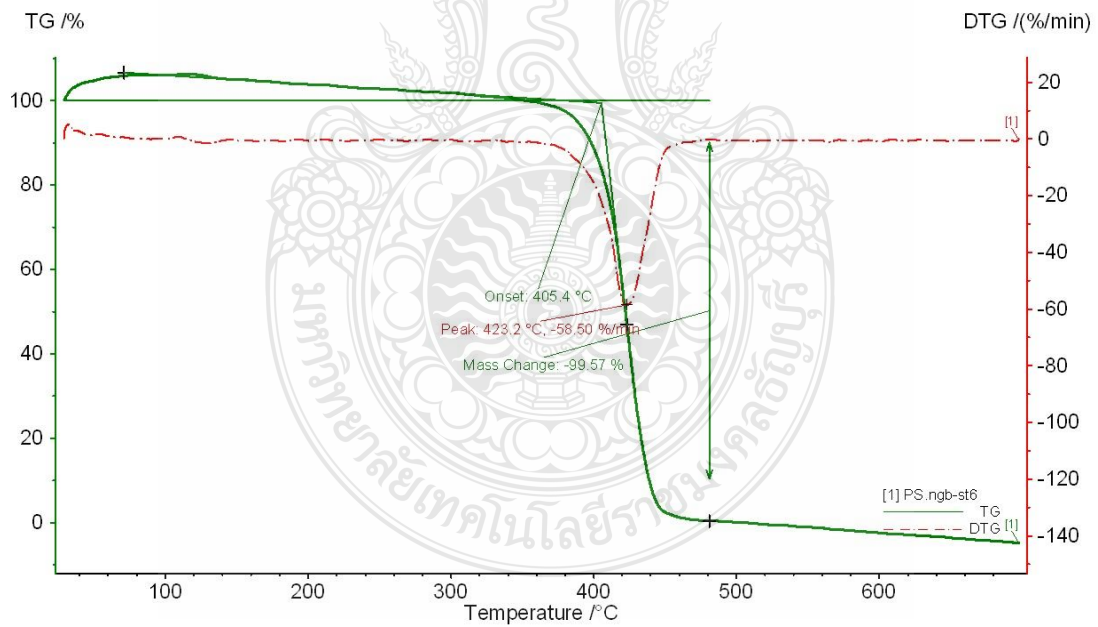


Figure 4.2 TGA curve of HDPE



**Figure 4.3** TGA curve of PP



**Figure 4.4** TGA curve of PS

## 4.2 Proximate and ultimate analyses of raw materials

Proximate and ultimate analysis of all materials were studied from previous work. These elements in raw materials affect the properties of combustion. The total mass of the species will decrease while burning. Carbon and hydrogen are the main components in hydrocarbon compounds, including plastic waste and used lubricant components that contain a small amount of oxygen from additives. Detection of the presence of hydrocarbons in raw materials can be determined from the H / C ratio. The H / C ratio also indicates the level of carbon-carbon bond saturation in liquid products. In the pyrolysis of oil products [32,33]. From Table 4.2, we found that PP has the highest H / C ash ratio, while PS shows the lowest H / C ratio and no ash content. H / O ratio of raw materials indicates that pyrolysis oil products are higher compared to raw materials. Oil shows the H / O ratio higher than plastic waste. The O / C ratio refers to the acidity of oil products. Low O / C ratio compounds showing low acidity Pyrolysis oil products show the rate of reduction of O / C in waste oil compared to the case of using PS as raw material.

**Table 4.2** Feedstock characteristics.

| Feed     | Proximate Analysis<br>(%wt.) |     |      | Ultimate Analysis (%wt.) |      |      |        |        |
|----------|------------------------------|-----|------|--------------------------|------|------|--------|--------|
|          | Volatile Matter              | Ash | C    | H                        | O    | H/C  | H/O    | O/C    |
| HDPE [2] | 99.4                         | 0.6 | 85.5 | 14.2                     | 0.44 | 1.99 | 516.4  | 0.0039 |
| PP [2]   | 99.1                         | 0.9 | 85.1 | 14.4                     | 1.06 | 2.03 | 217.4  | 0.0093 |
| PS [20]  | 99.5                         | 0.0 | 92.7 | 7.9                      | 0    | 1.02 | 104.6  | 0.0108 |
| Oil [11] | 98.88                        | 0.8 | 85.1 | 14.05                    | 0.15 | 1.98 | 1498.7 | 0.0013 |

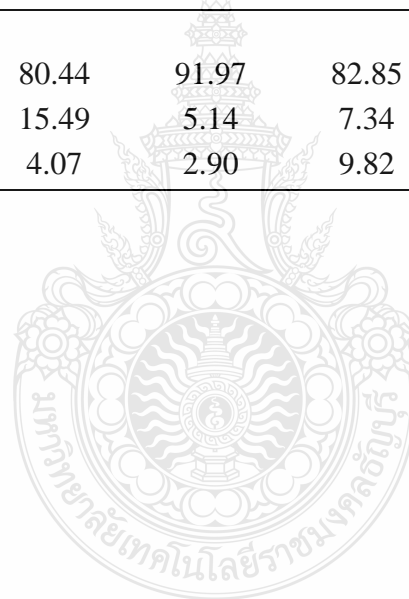
## 4.3 Effect of feedstock proportion

### 4.3.1 Proportion of waste lubricant oil with each waste plastic

Co-pyrolysis of Oil:HDPE mixtures were studied in proportions 100:0, 75:25, 50:50, 40:60 25:75, and 0:100 by weight. Co-pyrolysis of Oil:PS and Oil:PP mixtures were studied in proportions 100:0, 75:25, 60:40, 50:50, 40:60 25:75, and 0:100 by weight. The accumulation of liquid products stopped and no longer found the gas products in the system. The reactor was visually inspected to ensure the reaction was complete. The yield of solid products is determined by measuring the weight changes in the reactor, the yield of liquid products is determined by measuring the weight gain in the collected vessel. The yield of the gas product is determined by the mass balance and assumes that the mass of the sample is not proportional to the measurement of liquid and solid products from the system in the form of gas (Table 4.3).

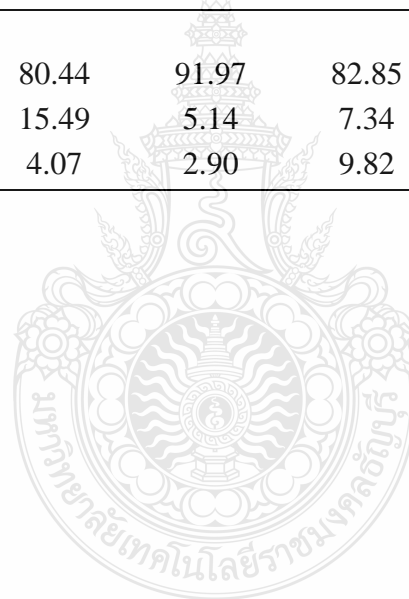
**Table 4.3** Properties and yield of Oil:HDPE [12]

| Property              | Oil:HDPE |       |       |       |       |       | Diesel standard |
|-----------------------|----------|-------|-------|-------|-------|-------|-----------------|
|                       | 100:0    | 75:25 | 50:50 | 40:60 | 25:75 | 0:100 |                 |
| Flash point (°C)      | 32.5     | 33.0  | 61.5  | 31.5  | 31.5  | 65.5  | >52 °C          |
| Viscosity (cSt) @40°C | 1.95     | 2.50  | 2.60  | 2.20  | 2.10  | 2.40  | 1.80-4.10       |
| Specific gravity      | 0.82     | 0.80  | 0.82  | 0.78  | 0.78  | 0.79  | 0.81-0.87       |
| Distillation °C @90%  | 297      | 268   | 250   | 276   | 288   | 290   | <357°C          |
| Color                 | 7.0      | 5.0   | 3.0   | 4.0   | 3.0   | 1.5   | <7.5            |
| % Yield               |          |       |       |       |       |       | -               |
| Oil                   | 73.86    | 80.44 | 91.97 | 82.85 | 92.05 | 84.42 |                 |
| Gases                 | 12.29    | 15.49 | 5.14  | 7.34  | 5.79  | 14.28 | -               |
| Solid                 | 13.75    | 4.07  | 2.90  | 9.82  | 2.17  | 1.30  | -               |



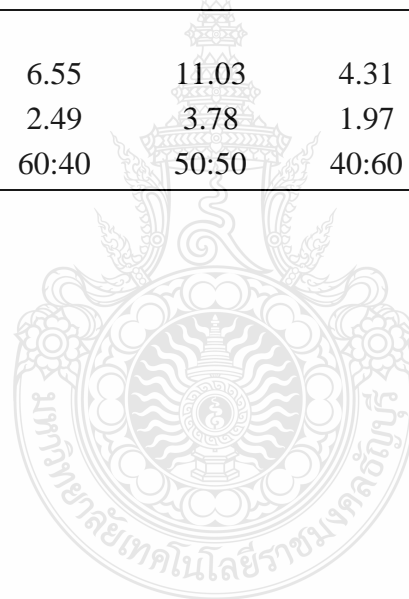
**Table 4.4** Properties and yield of Oil:PP [43]

| Property              | Oil:PP |       |       |       |       |       | Diesel standard |
|-----------------------|--------|-------|-------|-------|-------|-------|-----------------|
|                       | 100:0  | 75:25 | 50:50 | 40:60 | 25:75 | 0:100 |                 |
| Flash point (°C)      | 75:25  | 60:40 | 50:50 | 40:60 | 25:75 | 0:100 | >52 °C          |
| Viscosity (cSt) @40°C | 40.5   | 38    | 33    | 31    | 32    | 34    | 1.80-4.10       |
| Specific gravity      | 3.97   | 3.25  | 2.32  | 2.15  | 1.67  | 1.56  | 0.81-0.87       |
| Distillation °C @90%  | 0.81   | 0.81  | 0.76  | 0.763 | 0.77  | 0.76  | <357°C          |
| Color                 | 348    | 350   | 343   | 339   | 337   | 345   | <7.5            |
| % Yield               |        |       |       |       |       |       | -               |
| Oil                   | 73.86  | 80.44 | 91.97 | 82.85 | 92.05 | 84.42 |                 |
| Gases                 | 12.29  | 15.49 | 5.14  | 7.34  | 5.79  | 14.28 | -               |
| Solid                 | 13.75  | 4.07  | 2.90  | 9.82  | 2.17  | 1.30  | -               |



**Table 4.5** Properties and yield of Oil:PS [13]

| Property              | Oil:PS |       |       |       |       |       | Diesel standard |
|-----------------------|--------|-------|-------|-------|-------|-------|-----------------|
|                       | 75:25  | 60:40 | 50:50 | 40:60 | 25:75 | 0:100 |                 |
| Flash point (°C)      | 75:25  | 60:40 | 50:50 | 40:60 | 25:75 | 0:100 | >52 °C          |
| Viscosity (cSt) @40°C | 40.5   | 50    | 52    | 31    | 33    | 49    | 1.80-4.10       |
| Specific gravity      | 2.48   | 2.36  | 1.82  | 1.97  | 1.37  | 0.93  | 0.81-0.87       |
| Distillation °C @90%  | 0.841  | 0.875 | 0.867 | 0.893 | 0.861 | 0.937 | <357°C          |
| Color                 | 306    | 308   | 312   | n.d.  | n.d.  | n.d.  | <7.5            |
| % Yield               |        |       |       |       |       |       | -               |
| Oil                   | 18.48  | 6.55  | 11.03 | 4.31  | 5.61  | 2.74  |                 |
| Gases                 | 1.27   | 2.49  | 3.78  | 1.97  | 0.7   | 0.78  | -               |
| Solid                 | 75:25  | 60:40 | 50:50 | 40:60 | 25:75 | 0:100 | -               |



### **Effect of different ratio of oil with HDPE**

Five different ratios of waste lubricant oil on HDPE waste mixtures were tested: 100:0; 75:25; 50:50; 40:60; 25:75 and 0:100 by weight. Each of these wastes was subjected to a final temperature of 450°C for 4 hours. Oil product from 100:0 (only used lubricant oil) had all properties according to diesel standard except flash point temperature was below the standard. Table 4.2 shows the comparing properties of oil products, at ratio of 25:75 was the highest oil yield but flash point temperature unsatisfied on diesel standard. Only the ratio of 50:50 by weight of oil product was satisfied on diesel standard (flash point 61.5 °C, viscosity 2.60 cSt, specific gravity 0.82, distillation @90% (recovered) 250 °C and color 3.0).

### **Effect of different ratio of oil with PP**

Table 4.3 was showed results of pyrolytic oil properties from co-pyrolysis between used lubricant oil and PP, proportion that increased PP from ratio 50:50, 40:60 and 25:75 %wt had specific gravity less than diesel standard, all oil sample had flash point temperature below 52°C (diesel standard) but ratio 75:25 had the highest flash point (40.5°C). Color of all product oils not over 7.5 and only viscosity of ratio 25:75 was below diesel standard (1.8-4.1 cSt). Distillations @ 90% recovered of all pyrolytic oil were on-spec of diesel standard because they were not over temperature at 357°C. Therefore, ratio 75:25 is the best proportion, all properties except flash point be up to standard.

### **Effect of different ratio of oil with PS**

Period time of co-pyrolysis between used lubricating oil and PS with catalyst finished less than 4 hours. Flash point temperature of PS is 49°C closely diesel oil standard (>52°C) but specific gravity and viscosity were not on diesel oil standard. Studying of co-pyrolysis with proportions between used oil and PS were showed only ratio 50:50 was showed all properties on diesel standard such as flash point is 52°C, specific gravity is 0.867, color is 2.5-3, viscosity@40°C is 1.82 cSt and distillation@90% recovered is 311.6°C. The results were showed when increasing of PS proportion oil yield increased (80-93 %wt); gases yield have in range 4.31-18.25 %wt.; solid yield have in range 0.7-3.78 %wt. For 40:60, 25:75, and 0:100 proportions cannot test distillation property



because bubble occur and overflow through condenser; specific gravity and viscosity were not on diesel standard (Table 4.4).

**Table 4.5.** Percentage compounds of pyrolytic oil by GC-MS.

| Pyrolysis       | Linear paraffins < C <sub>24</sub> | Linear and branched paraffins > C <sub>24</sub> | Double bonds compounds | Cyclic compounds | Aromatic compounds |
|-----------------|------------------------------------|---|------------------------|------------------|--------------------|
| <b>Oil only</b> |                                    |   |                        |                  |                    |
| 100:0           | 55.60                              | 24.51   | 9.82                   | 9.97             | 0.10               |
| 100:0*          | 27.65                              | 12.03   | 18.77                  | 41.36            | 0.19               |
| <b>Oil:HDPE</b> |                                    |   |                        |                  |                    |
| 50:50           | 58.691                             | 13.733  | 26.112                 | 1.463            | -                  |
| 25:75           | 57.775                             | 6.370   | 34.711                 | 1.124            | -                  |
| 0:100           | 55.282                             | 4.649   | 37.823                 | 2.247            | -                  |
| <b>Oil:PS</b>   |                                    |   |                        |                  |                    |
| 75:25           | 46.61                              | 3.95  | 19.09                  | 6.46             | 23.89              |
| 60:40           | 31.39                              | 7.08  | 12.78                  | 14.76            | 33.99              |
| 50:50           | 31.01                              | 18.07   | 7.95                   | 6.42             | 36.55              |
| 40:60           | 26.20                              | 11.26   | 6.48                   | 19.64            | 36.42              |
| 0:100           | 25.39                              | 1.01  | 16.56                  | 17.45            | 39.59              |
| 0:100*          | 13.37                              | -   | 14.89                  | 12.80            | 58.94              |
| <b>Oil:PP</b>   |                                    |   |                        |                  |                    |
| 75:25           | 54.98                              | 12.68   | 17.94                  | 13.83            | 0.57               |
| 60:40           | 47.85                              | 16.76   | 18.65                  | 15.74            | 1.0                |
| 50:50           | 43.22                              | 18.88   | 19.32                  | 18.58            | -                  |
| 40:60           | 35.40                              | 21.12   | 20.44                  | 23.04            | -                  |
| 0:100           | 32.19                              | 11.73   | 24.42                  | 28.15            | 3.51               |
| 0:100*          | 27.65                              | 12.03   | 18.77                  | 41.36            | 0.19               |

### Hydrocarbon compounds

The hydrocarbon compounds were analyzed by using GC-MS. Pyrolytic oils have a lot of chemicals more than 400 chemicals therefore they were grouped based on structure in 5 groups: linear paraffins < C<sub>24</sub>; linear and branched paraffins > C<sub>24</sub>; double bonds compounds; cyclic compounds; and aromatic compounds. Four ratios of oil and HDPE (types of oil products) were selected for chemical compositions analysis by GC-MS as shown in Table 4.5. For comparison purpose, peaks were categorized into five groups: linear paraffins lower than C<sub>24</sub>, linear and branched paraffins higher than C<sub>24</sub>, compounds

with double bonds, cyclic compounds (aliphatic hydrocarbons with cyclic structure) and aromatic compounds (eg. Benzene derivatives and PAHs) As shown in Table 4.5, most of peaks were identified as Linear paraffins lower than  $C_{24}$  for oil product at the ratio of 50:50 and subsequent by hydrocarbon compound with double bonds, linear and branched paraffins of higher than  $C_{24}$  and cyclic compounds while aromatic compound was not identified in all oil samples. Increasing in HDPE quantity effected in decreasing of linear paraffins  $< C_{24}$  and linear and branched paraffins  $> C_{24}$ . The pyrolysis oil of ratio 50:50 by weight provides higher liner paraffin compound compare to the oil of ratio 25:75 by weight. Therefore, flash point and viscosity of oil from the ratio 50:50 by weight had higher than the ratio 25:75 by weight. Co-pyrolysis of used lubricant oil and PS was showed when proportion of used lubricant oil increasing as a result linear paraffins  $< C_{24}$  increased. In other hand, increasing of PS effect linear paraffins  $< C_{24}$  decreased and aromatic compound increased.

Aromatic compound was found in monomer structure not found in form of dimer and trimer structures. Proportion 75:25, 60:40 and 50:50 were detected high quantity of linear and branched paraffins  $> C_{24}$  and aromatic compounds that effecting in properties of oil products such as flash point, viscosity, specific gravity, and distillation be up to diesel standard. 50:50 ratio had the highest flash point effects high linear and branched paraffins  $> C_{24}$  (18.07%).

The most composition of oil products from co-pyrolysis between used lubricant oil and PP were linear paraffins  $< C_{24}$ , they were decreased when amount of PP increased while linear and branched paraffins  $> C_{24}$ , double bonds compounds and Cyclic compounds were increased. Proportion 75:25 and 60:40 were showed aromatic compounds not more than 1.0% and high quantity of linear paraffins  $< C_{24}$ , 54.98% and 47.85%, respectively. Pyrolytic oil from used lubricant non-catalyst pyrolysis were found low amount of linear paraffins  $< C_{24}$  (27.65%) and linear and branched paraffins  $> C_{24}$  (12.03%) comparison with catalyst pyrolysis had high amount of linear paraffins  $< C_{24}$  (55.60%) and linear and branched paraffins  $> C_{24}$  (24.51%). The GC-MS curves of co-pyrolysis as shown in Figure 4.5 to Figure 4.8.

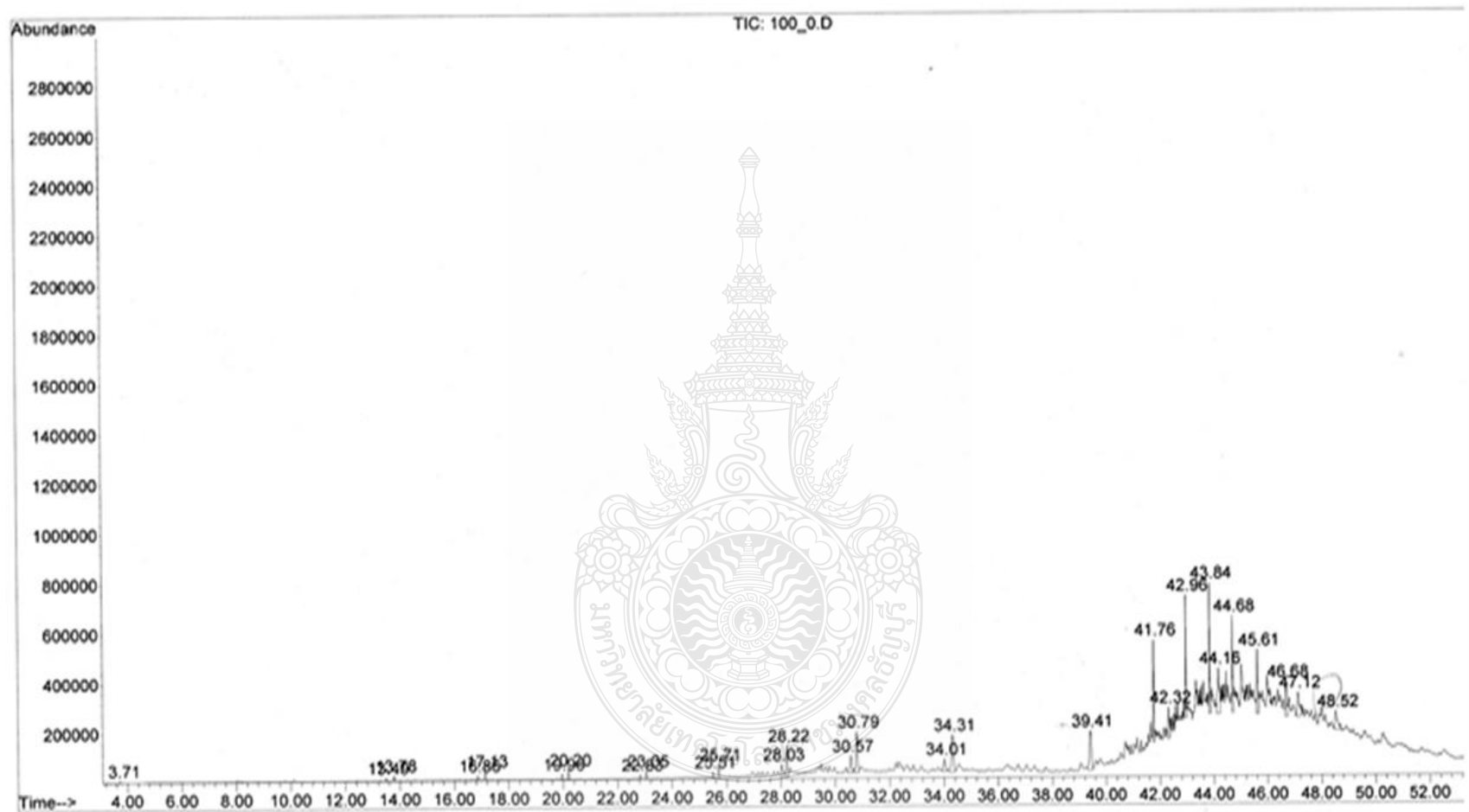


Figure 4.5 Hydrocarbon analysis of co-pyrolytic oil at Oil:HDPE ratio 100:0 by weight

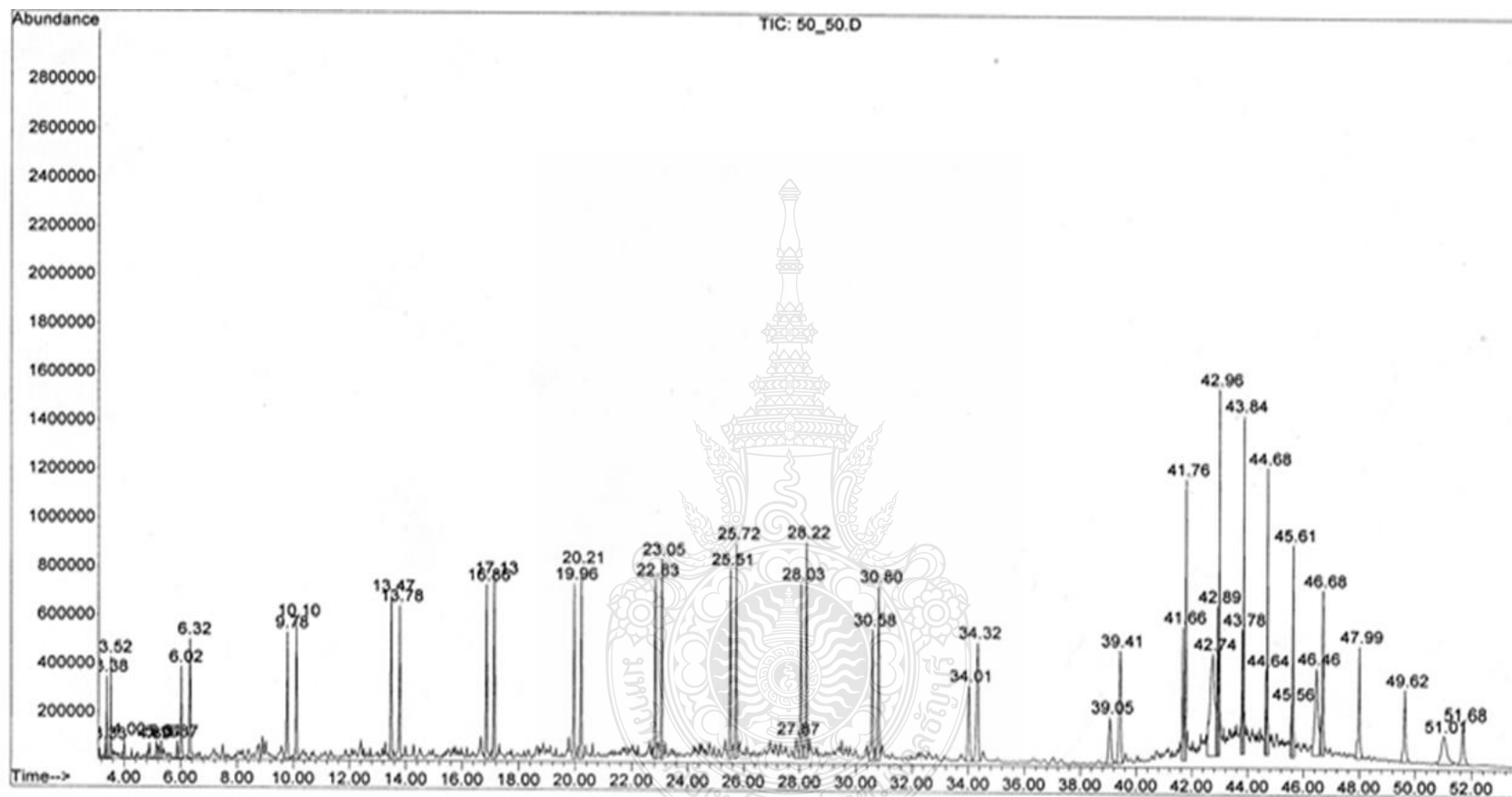


Figure 4.6 Hydrocarbon analysis of co-pyrolytic oil at Oil:HDPE ratio 50:50 by weight

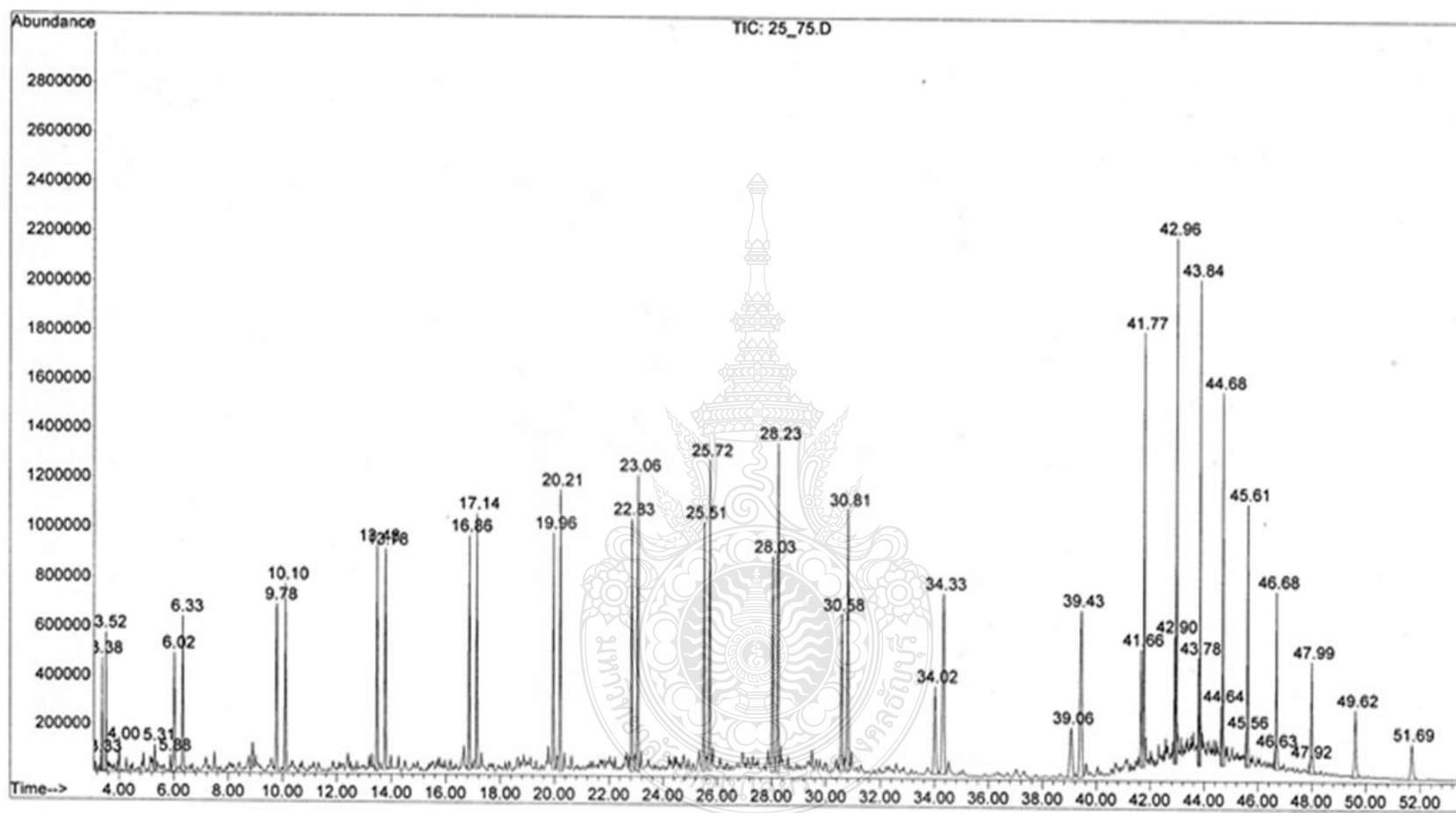
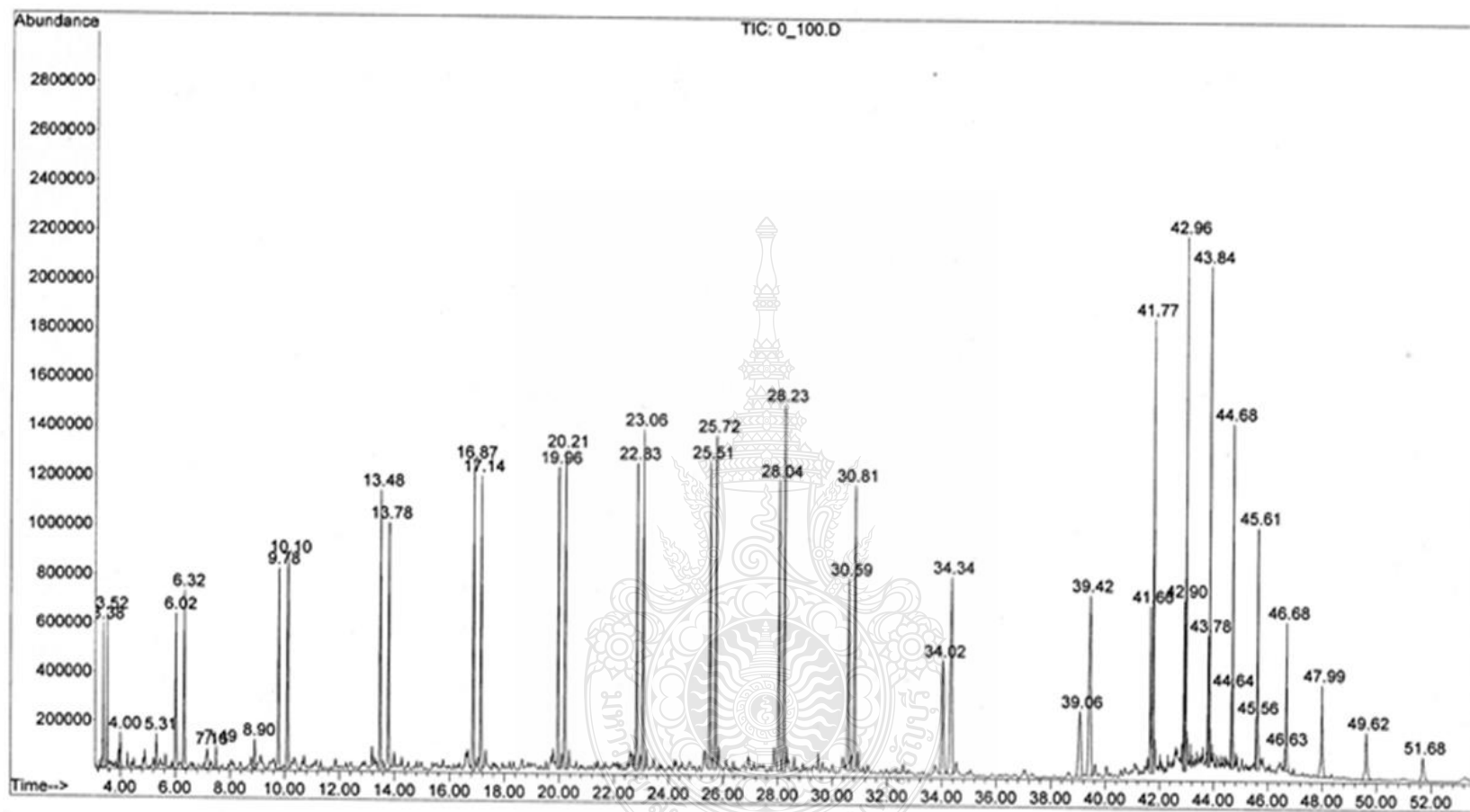
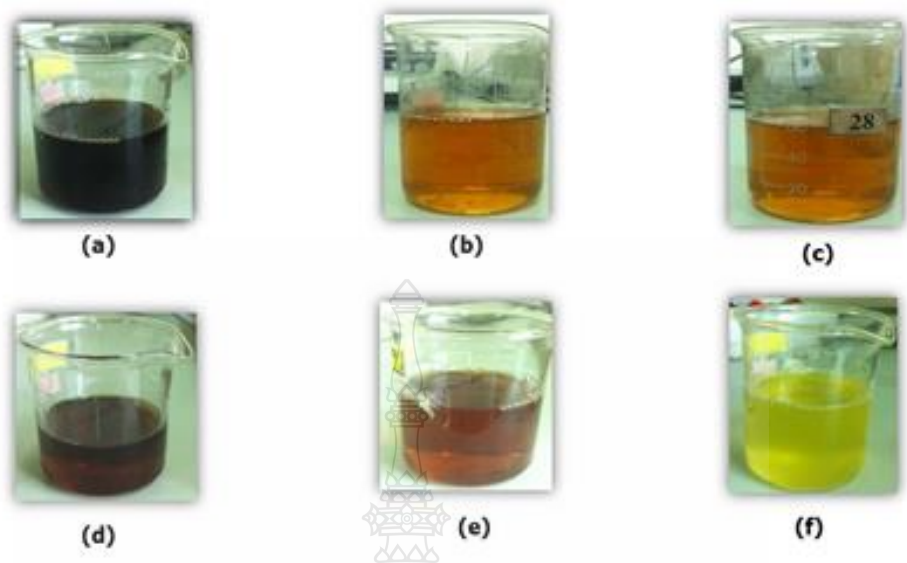


Figure 4.7 Hydrocarbon analysis of co-pyrolytic oil at Oil:HDPE ratio 25:75 by weight

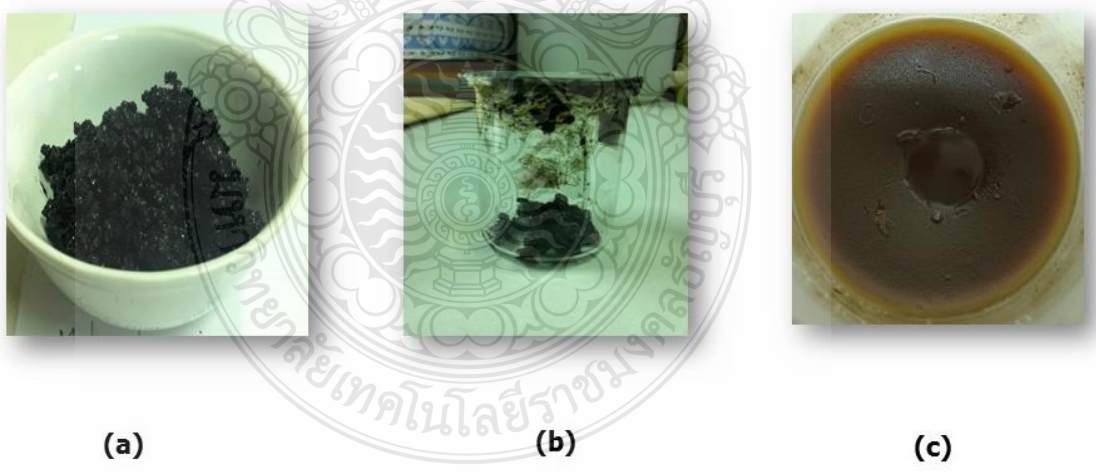


**Figure 4.8** Hydrocarbon analysis of co-pyrolytic oil at Oil:HDPE ratio 0:100 by weight



**Figure 4.9** Co-pyrolytic oil between waste oil and HDPE

(a) 100:0 (b) 25:75 (c) 40:60  
 (d) 50:50 (e) 75:25 (f) 0:100



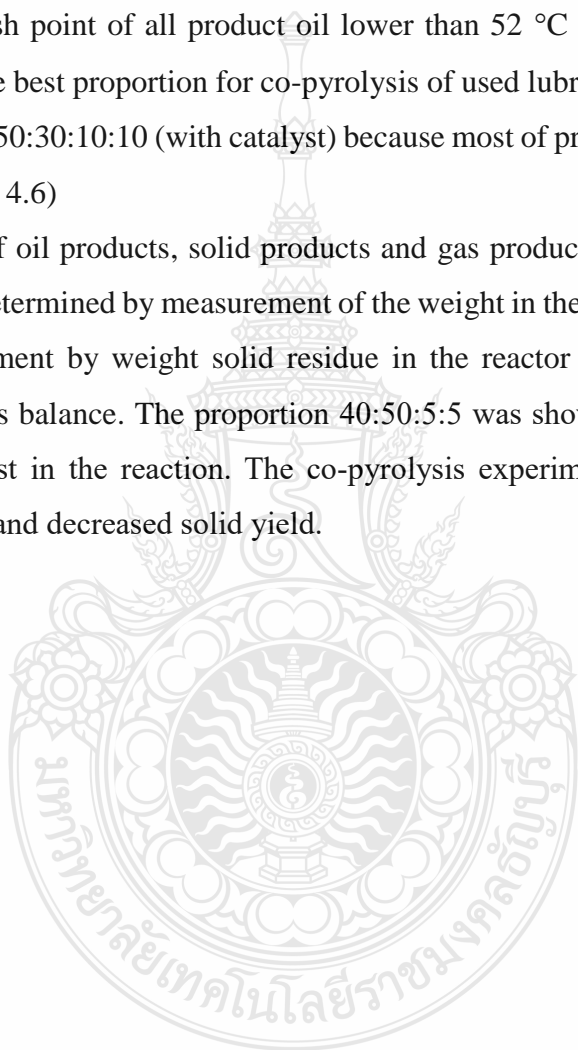
**Figure 4.10** Solid products from co-pyrolysis (Oil:HDPE)

(a) 100:0 (b) 50:50 (c) 0:100

#### 4.3.2 Proportion of waste lubricant oil with 3 types of waste plastic

Co-pyrolysis of used lubricant oil and mixed plastic wastes (HDPE, PP, and PS) were studied in proportions 50:30:10:10, 40:50:5:5, 20:60:20:0 by with and without catalyst. All proportions cannot show the distillation value and cetane index because when heated oil product as boiling point, many bubble had occurred and overflow to condenser of apparatus. Viscosity and color of product oils followed diesel standard. On the other hand, flash point of all product oil lower than 52 °C that mean not followed diesel standard. The best proportion for co-pyrolysis of used lubricant oil and three types of plastic wastes is 50:30:10:10 (with catalyst) because most of properties followed diesel standard (see Table 4.6)

The yield of oil products, solid products and gas products were shown in Table 4.7, oil yield was determined by measurement of the weight in the collected vessels. Solid yield can measurement by weight solid residue in the reactor and gaseous yield was determined by mass balance. The proportion 40:50:5:5 was shown the highest oil yield and without catalyst in the reaction. The co-pyrolysis experimental with catalyst can increased oil yield and decreased solid yield.





**Table 4.6** Properties and yield of co-pyrolysis with 3 types of waste plastic

| Properties                       | Oil:PE:PP:PS (%wt) |              |              |               |            |             | Diesel standard |
|----------------------------------|--------------------|--------------|--------------|---------------|------------|-------------|-----------------|
|                                  | 50:30:10:10        | 50:30:10:10* | 40:50: 5 : 5 | 40:50: 5 : 5* | 20:60:20:0 | 20:60:20:0* |                 |
| Flash point (°C)                 | 29.25              | 31.5         | 27.0         | 29.7          | 28.0       | 28.75       | >52             |
| Viscosity @ 40°C (cSt)           | 2.301              | 2.211        | 3.215        | 2.981         | 2.792      | 2.520       | 1.8 - 4.1       |
| Specific gravity @ 60°F          | 0.85               | 0.82         | 0.81         | 0.82          | 0.80       | 0.79        | 0.81 - 0.87     |
| Distillation @ 90% recovery (°C) | n.d.               | n.d.         | n.d.         | n.d.          | n.d.       | n.d.        | <357            |
| Colour                           | 1.5                | 1.5          | 1.5          | 2.0           | 1.5        | 1.5         | <4.0            |
| Cetane index                     | n.d.               | n.d.         | n.d.         | n.d.          | n.d.       | n.d.        | >50             |

**Table 4.7** Product yield of co-pyrolysis with 3 types of waste plastic

| %Yield       | Oil:HDPE:PP:PS (%wt.) |              |              |               |            |             |
|--------------|-----------------------|--------------|--------------|---------------|------------|-------------|
|              | 50:30:10:10           | 50:30:10:10* | 40:50: 5 : 5 | 40:50: 5 : 5* | 20:60:20:0 | 20:60:20:0* |
| <b>Oil</b>   | 73.41                 | 84.58        | 85.57        | 87.23         | 79.40      | 88.60       |
| <b>Solid</b> | 14.80                 | 5.88         | 5.05         | 4.40          | 10.50      | 9.71        |
| <b>Gases</b> | 11.79                 | 9.54         | 9.38         | 8.37          | 10.20      | 1.70        |

\*Used catalyst

#### 4.3.3 Proportion of waste lubricant oil with 2 types of waste plastic

Three different ratios of waste lubricant oil on two type of waste plastics were tested: 50:30:20:0, 50:30:0:20, and 50:0:30:20 percentage by weight. Each experiments were subjected to a final temperature of 450°C for 4 hours. Table 4.8 shows the comparing properties of oil products, at ratio of 50:30:0:20 was the highest oil yield. All experiments were provided flash point temperature unsatisfied on diesel standard (lower than 52°C). The proportion of high content HDPE may increase flash point compared with PP and PS, respectively. The flash point of pyrolysis oil from PP and PS were lower than standard of diesel [34,35]. Specific gravity and color of the most ratio on diesel standard but distillation at 90% recovered and cetane index was shown only from ratio 50:30:20:0 as 353°C and 65, respectively. Because of the cause from polystyrene when oil samples were heated it had some bubble overflow into the condenser of the distillation tester also cetane index cannot reported. Both of cetane index or diesel index evaluate the ignition quality of diesel fuel from HDPE and PP pyrolysis oils [32,33].

Table 4.9 shows product productivity All experimental products show unsatisfactory flash point temperatures. (Below the standard 52 ° C) Higher HDPE content compared to PP and PS may increase the flash point. The flash point of pyrolysis oil obtained from PP and PS is lower than commercial diesel [33,34]. Specific gravity and color of the product resulting from all test ratios meet diesel standards. Previous research reported that pyrolysis of a mixture of PE, PP and waste oil (WMO) at different mixing ratios is 1: 1: 1, 1: 1: 2 and 1: 1: 4. By weight, increasing the amount of WMO in all combinations leads to an increase in both viscosity and specific gravity of liquid products. The flash point of all liquid products obtained from the co-pyrolysis process is lower than the commercial diesel (> 55 ° C) [11]. The distillation temperature at 90% recovery and the cetane index is shown only for the 50:30:20:0 (353 ° C and 65, respectively). This is because when the oil sample is heated due to the presence of styrene causing the overflow bubble in the condenser of the distillation test machine that still prevents indexing C Farnsworth Both the cetane index and diesel index are used to evaluate the combustion quality of diesel oil from HDPE and PP pyrolysis oil [35,36].

The oil from the laboratory shows that the impact of plastic waste in the mixture mixed with the lubricant used is as follows: PE / PS > PE / PP / PS > PP / PS which is similar to PE / PP. The gas is as follows: PP / PS > PE / PP > PE / PP / PS > PE / PS and stable yields are as follows: PE / PP > PE / PS > PE / PP / PS The trend of return of that product Close to the report by Miandad *et al.* [37].



**Table 4.8** Properties and yield of co-pyrolysis with 2 types of waste plastic

| Properties                     | Oil:PE:PP:PS (%wt.) |            |            | Diesel standard |
|--------------------------------|---------------------|------------|------------|-----------------|
|                                | 50:30:20:0          | 50:30:0:20 | 50:0:30:20 |                 |
| Flash point (°C)               | 29                  | 28         | 28         | >52             |
| Viscosity (cSt) @ 40 °C        | 1.98                | 2.20       | 2.25       | 1.8-4.1         |
| Specific gravity               | 0.81                | 0.82       | 0.82       | 0.81-0.87       |
| Distillation °C @ 90% recovery | 353                 | n.d.       | n.d.       | <357            |
| Colour                         | 2.5                 | 2.0        | 2.0        | <4.0            |
| Cetane index                   | 65                  | n.d.       | n.d.       | >50             |

n.d. = not detected. \*Standard of diesel specified by the Department of Energy Business, Ministry of Energy of Thailand.

**Table 4.9** Product yield of co-pyrolysis with 2 types of waste plastic

| % Yield; | Oil:HDPE:PP:PS (%wt.) |            |            |
|----------|-----------------------|------------|------------|
|          | 50:30:20:0            | 50:30:0:20 | 50:0:30:20 |
| Oil      | 63.36                 | 84.58      | 55.54      |
| Solid    | 18.22                 | 9.54       | 28.11      |
| Gases    | 18.42                 | 5.88       | 16.35      |

#### 4.4 Hydrocarbon Compounds

The oil products from the co-pyrolysis laboratory were examined for hydrocarbon compounds using gas chromatography - mass spectrometer (GC-MS). Oil products consist of more than 100 chemical components. Therefore, these compounds were grouped into four groups based on their structure: paraffin, olefin, cyclic, and aromatic compounds. The proportions of the four types of co-pyrolysis products as determined by GC-MS are shown in Table 4.10. The main component of standard diesel oil is paraffin for proportion 50:30:10:10 and 50:30:20:0. Aromatic compounds were found from proportion that high content of polystyrene. Oil products of ingredients with a ratio of 50: 30: 20: 0 showed the highest amount of paraffin (55.723%) in the total aliphatic compound oil products, 91.086% and no aromatic compounds because there was no PS in the raw materials. HDPE and PP are polyolefin plastic. It was found that olefins and cyclic compounds were used in the ingredients of the product 50: 30: 20: 0, probably because the heat value in the reactor was not enough to destroy the carbon bond of the raw material [38,39]

Siddiqui *et al.* Study the pyrolysis heat of four types of plastics (LDPE, HDPE, PP and PET) mixed with PS. They found that the oil products from PS pyrolysis are contained in the ingredients that produce the products. Romance controlled by styrene monomer and styrene oligomer. Most aliphatic compounds in oil are HDPE / PP / PS, followed by HDPE / PS and PP / PS, while oil products from PP / PS have the highest aromatic compounds, followed by HDPE / PS and HDPE. / PP / PS this work [40]

**Table 4.10** Hydrocarbon compounds in the product oils.

| Oil | Proportion %wt. |    |    | %Hydrocarbon Compound |         |        |          |
|-----|-----------------|----|----|-----------------------|---------|--------|----------|
|     | PE              | PP | PS | Paraffins             | Olefins | Cyclic | Aromatic |
| 50  | 30              | 10 | 10 | 44.450                | 23.576  | 4.134  | 27.840   |
| 50  | 30              | 20 | 0  | 55.723                | 35.363  | 8.914  | 0        |
| 50  | 30              | 0  | 20 | 35.096                | 18.540  | 0      | 46.364   |
| 50  | 0               | 30 | 20 | 10.365                | 6.897   | 14.523 | 68.215   |

#### 4.5 Number of Carbon Atoms

Another important parameter used to inspect oil products in diesel fuel is the number of carbon atoms in the composition of oil products. [41] Pyrolysis joint product analysis is shown in Table 4.11. For this work, the number of carbon atoms is divided into three phases: gasoline (C6-C12), diesel oil (C13-C19) and heavy oil (> C20). 20: 0 (45.28%); This mixture has a low amount of gasoline. Results confirm that the properties of the oil products of this mixture are fuel-like diesel. The highest diesel fuel fraction is studied using HDPE. Pyrolysis oil is similar to diesel fuel and contains hydrocarbon chains. Most straight lines are distributed in the range C10-C38. [42]. Therefore, it is advisable to use a high HDPE ratio for mixing plastics to produce diesel oil 10 from 50: 0: 30: 20 with the highest gasoline content, 50: 30: 10: 10 ratios, with heavy oil content and the highest balance of gasoline and diesel oil.

**Table 4.11** Proportion of compounds with different numbers of carbon atoms in the co-pyrolysis products.

| <b>Proportion<br/>(%wt.)<br/>Oil:PE:PP:PS</b> | <b>% Gasoline Oil<br/>Compounds<br/>(C<sub>6</sub>-C<sub>12</sub>)</b> | <b>% Diesel Oil<br/>Compounds<br/>(C<sub>13</sub>-C<sub>19</sub>)</b> | <b>% Heavy Oil<br/>Compounds<br/>(&gt;C<sub>20</sub>)</b> |
|---|--|---|---|
| 50:30:10:10                                   | 38.64  | 38.61   | 22.75   |
| 50:30:20:0                                    | 41.86  | 45.28   | 12.86   |
| 50:30:0:20                                    | 54.96  | 36.46   | 8.58  |
| 50:0:30:20                                    | 81.32  | 15.46   | 3.22  |

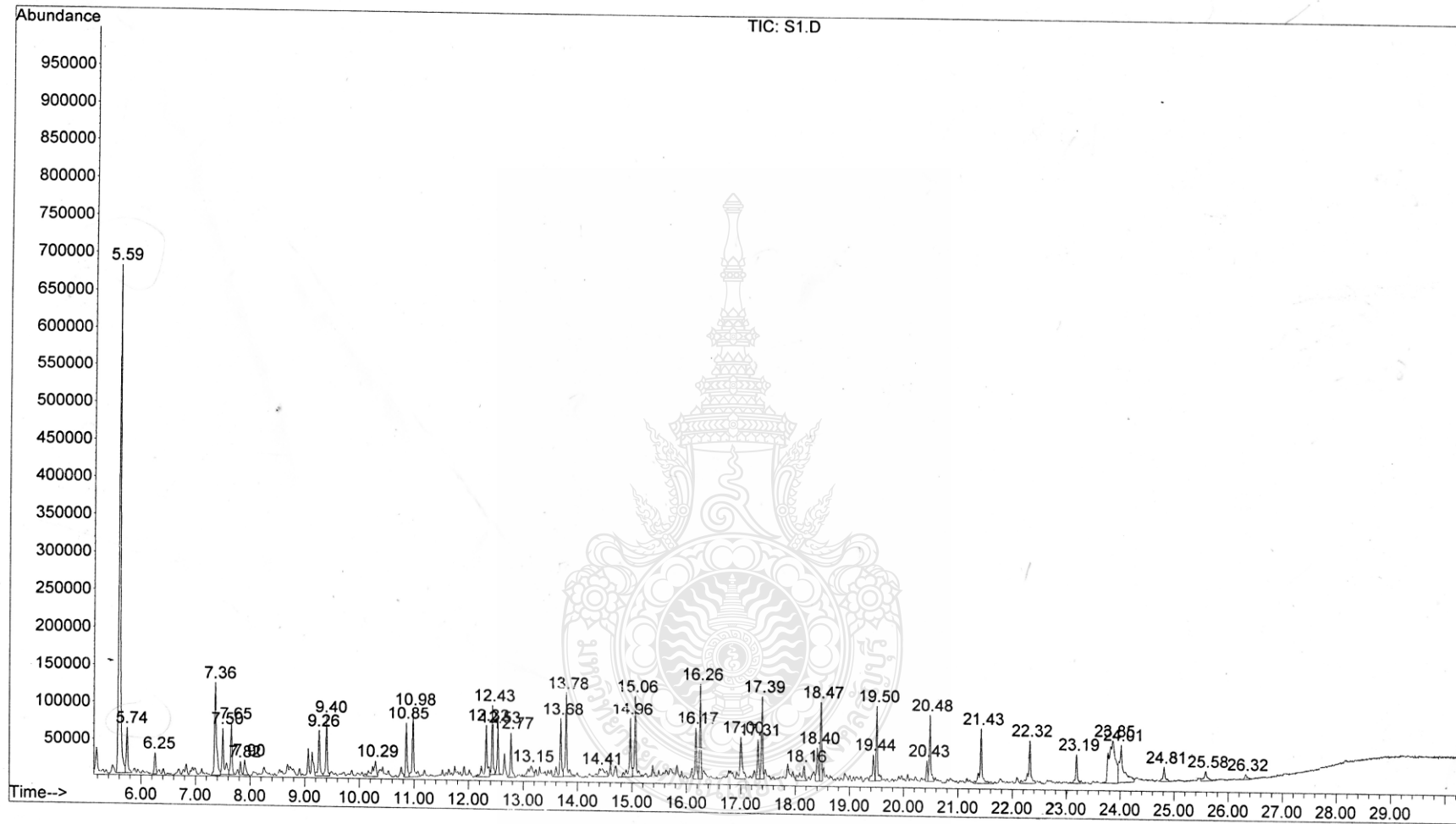
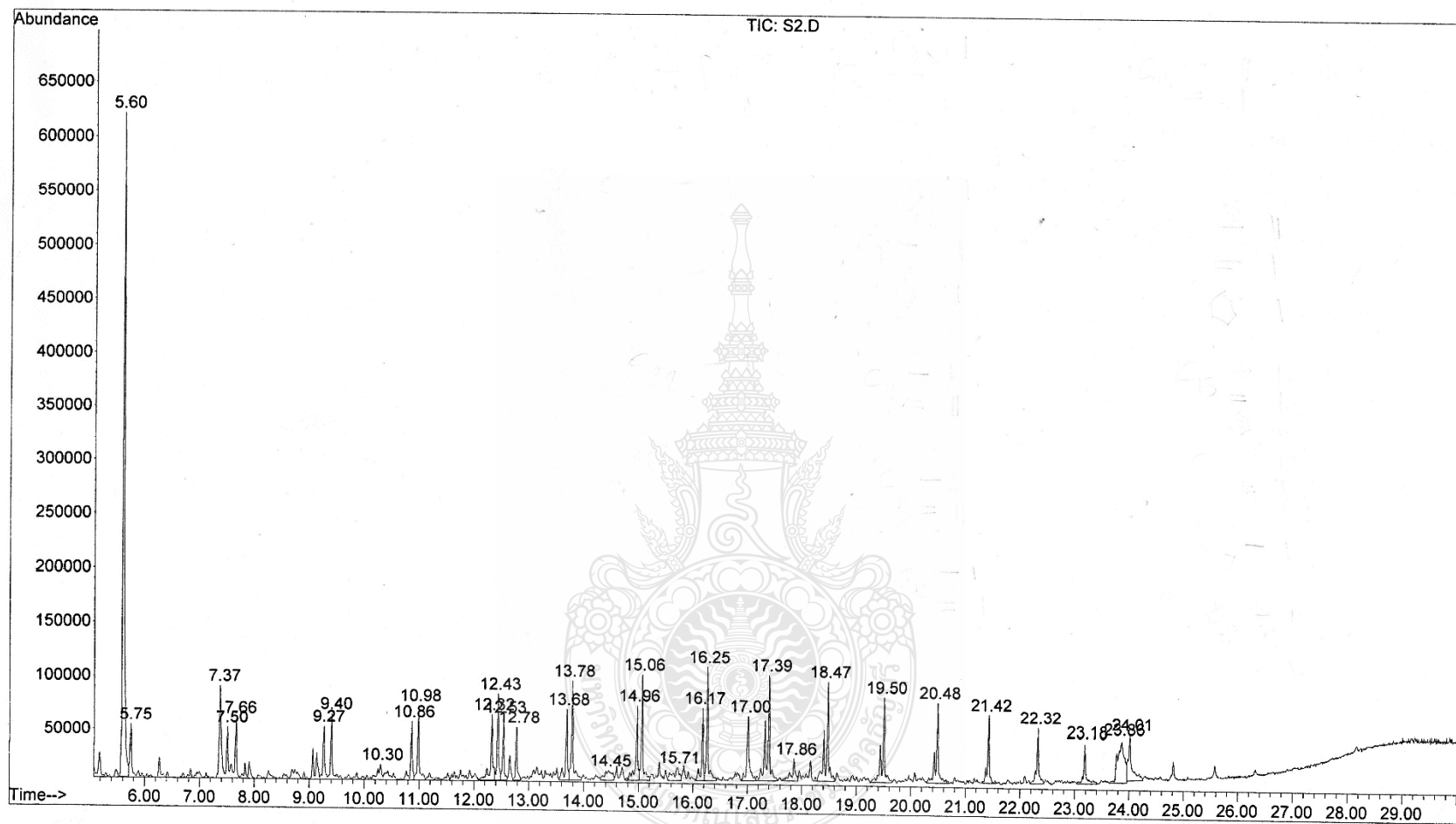


Figure 4.11 GC-MS curve of 50:30:10:10 (no catalyst) from lab-scale



**Figure 4.12** GC-MS curve of 50:30:10:10 (used catalyst) from lab-scale



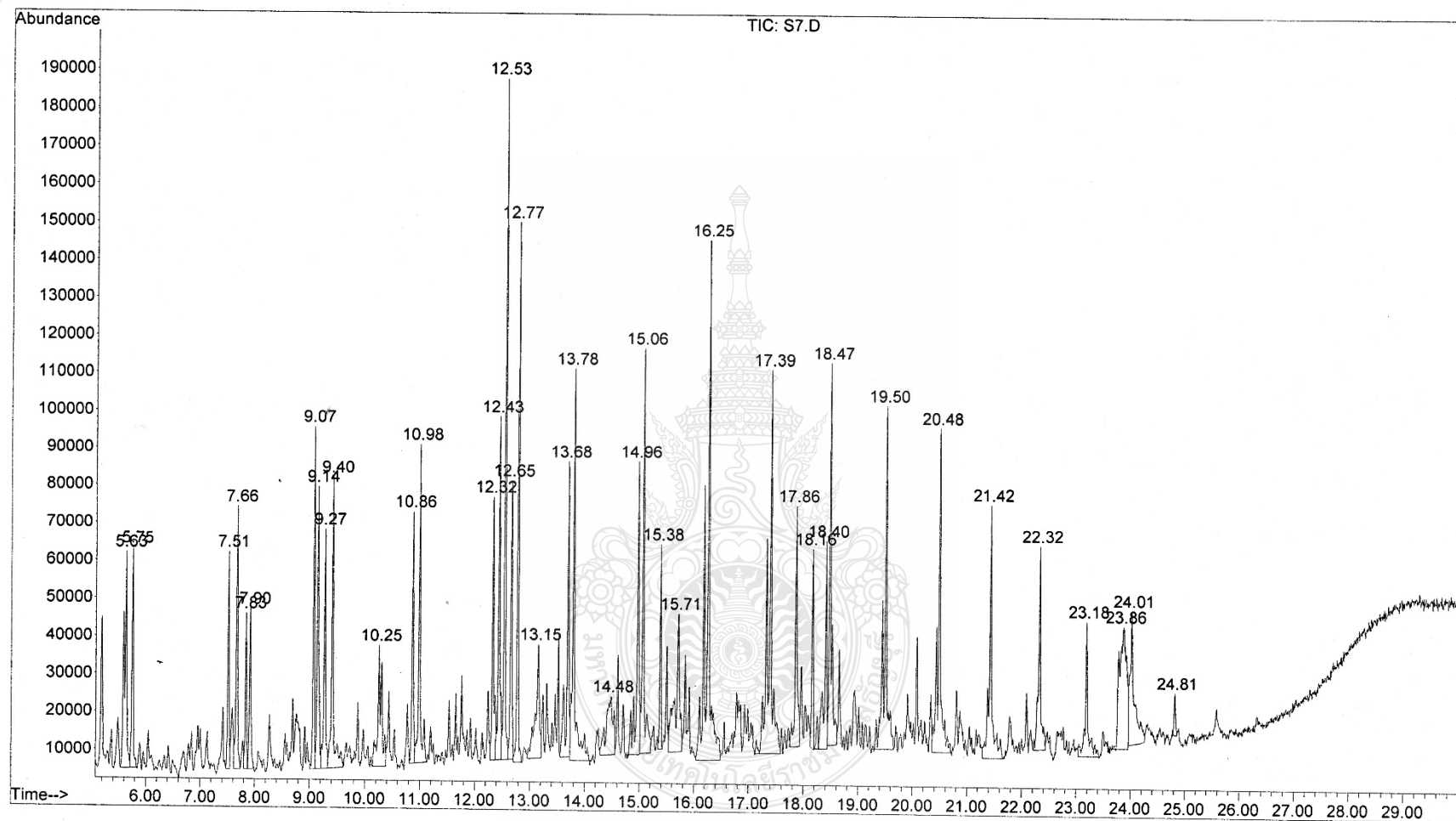


Figure 4.13 GC-MS curve of 50:30:20:0 (no catalyst) from lab-scale

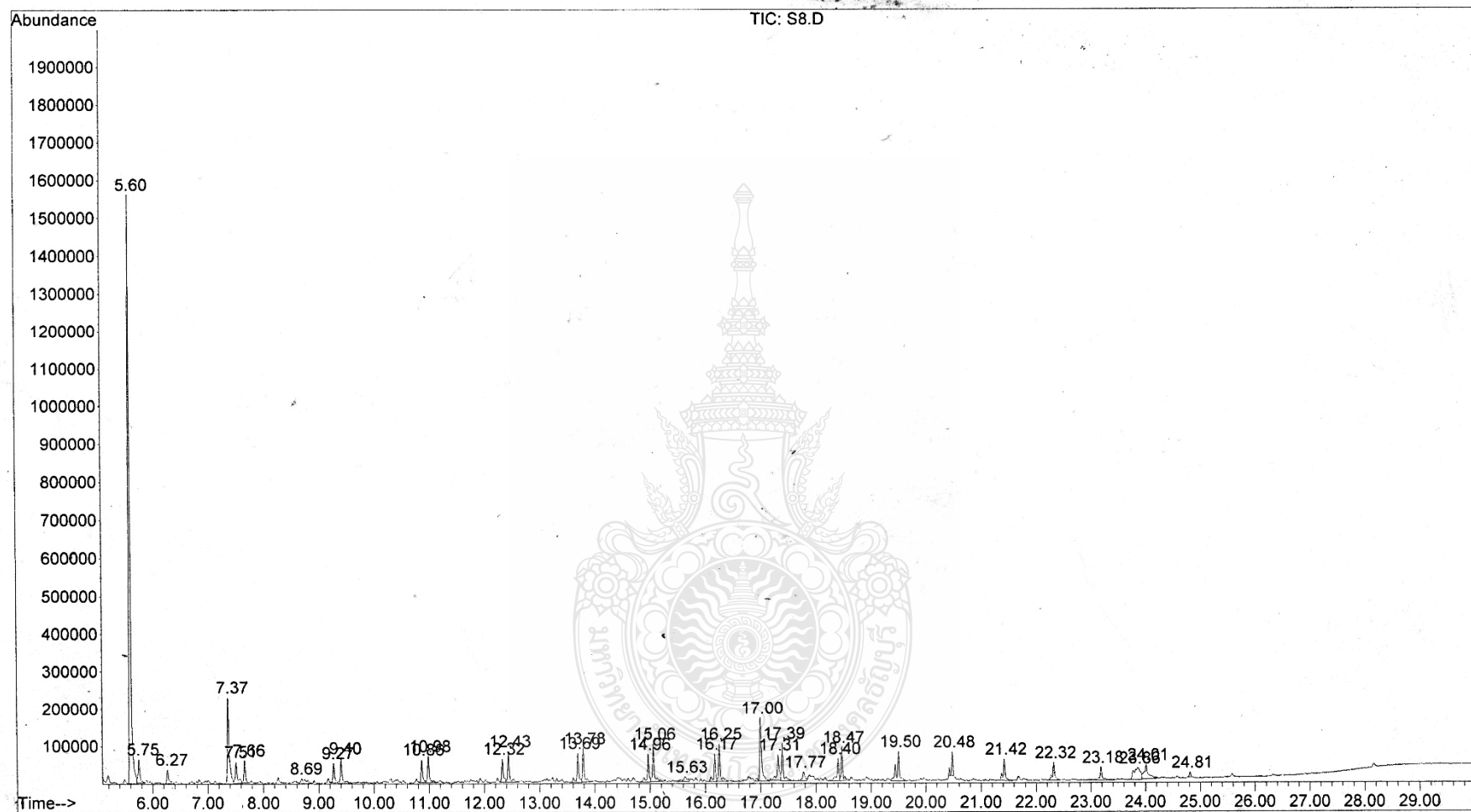


Figure 4.14 GC-MS curve of 50:30:0:20 (no catalyst) from lab-scale

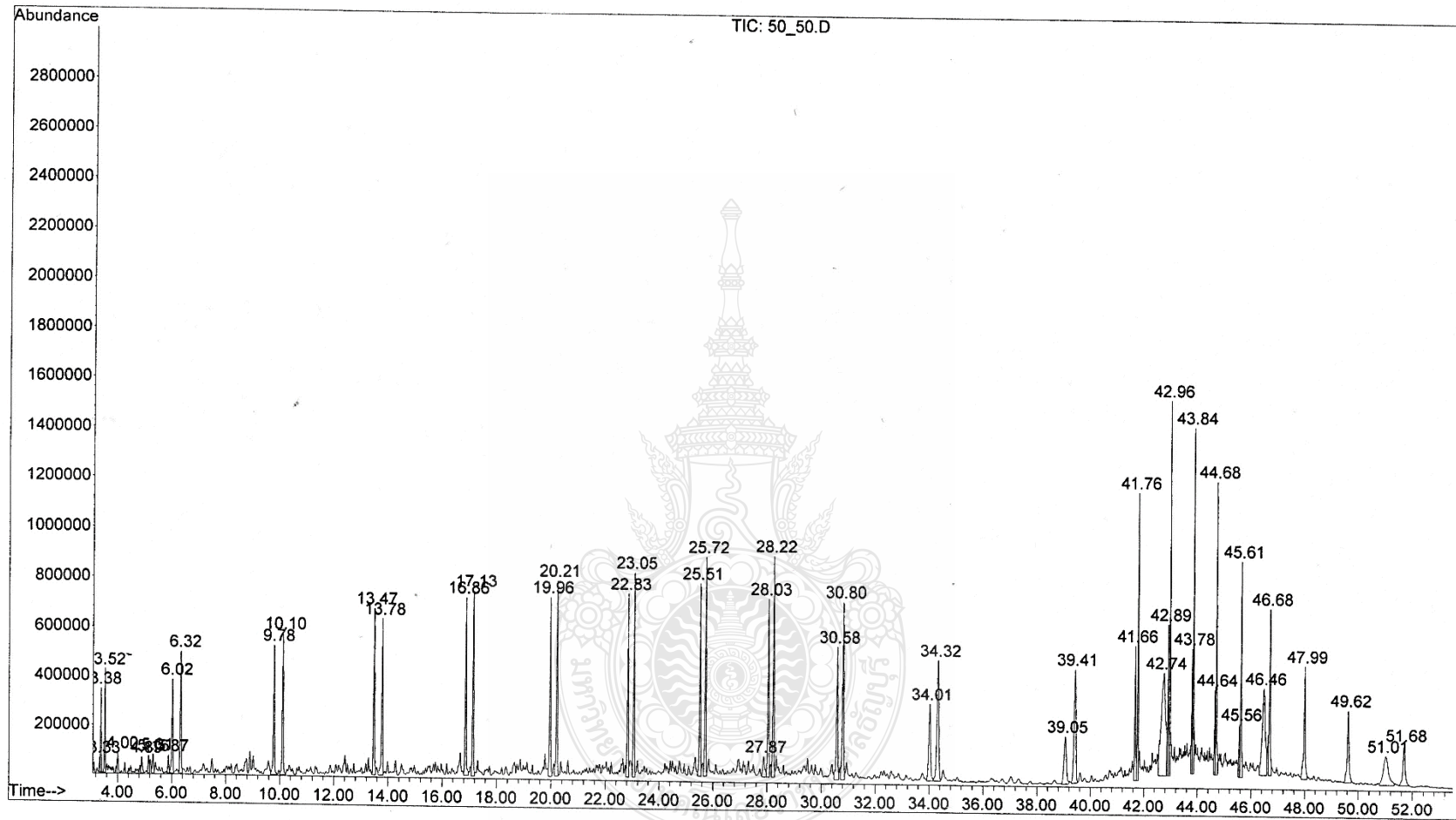
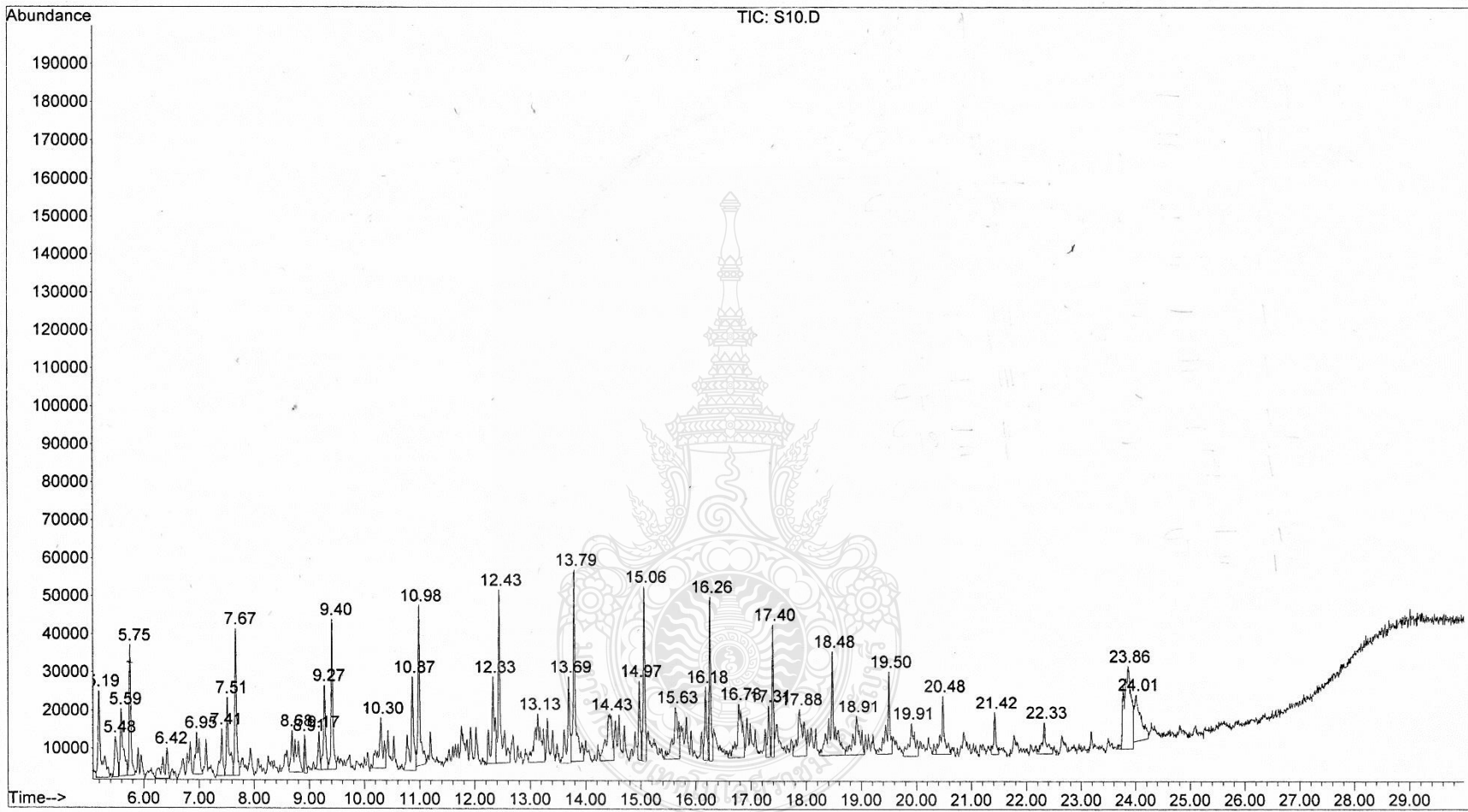


Figure 4.15 GC-MS curve of 50:50 of Oil :PE (no catalyst) from lab-scale



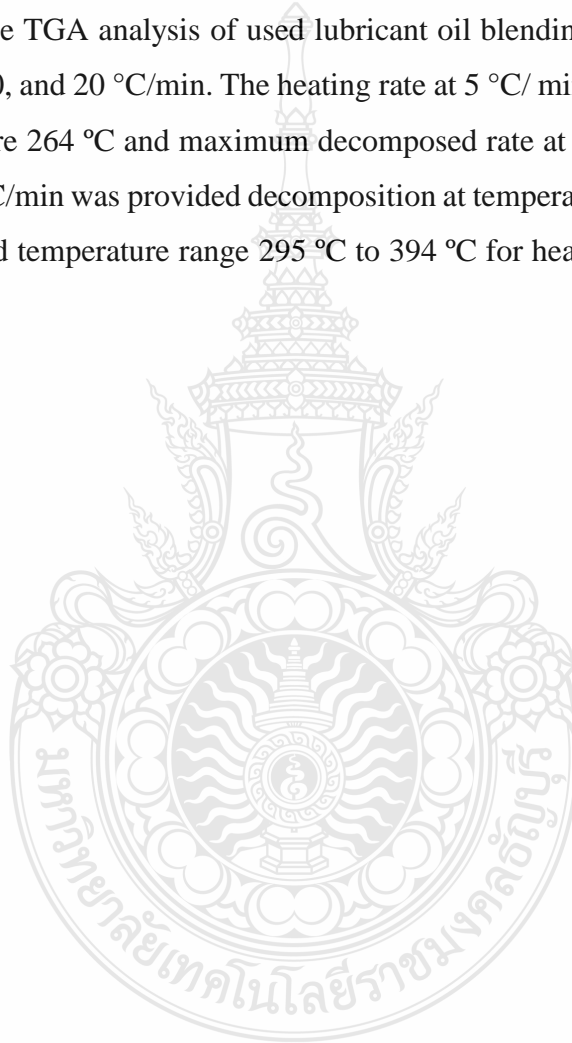
**Figure 4.16** GC-MS curve of 50:50 of Oil :HDPE (no catalyst) from prototype

## 4.6 Kinetic of co-pyrolysis

Kinetic of co-pyrolysis used lubricant oil and each types of plastic waste in lab scale were studied in this research by using TGA analytical. TGA curves of co-pyrolysis used lubricant oil and three type o plastics: Oil:PE, Oil:PP, and Oil:PS were used difference heating rate such as: 5, 10 and 20 °C/min.

### 4.6.1 Kinetic of Lubricant oil and of polypropylene

Based on the TGA analysis of used lubricant oil blending with polypropylene at heating rate of 5, 10, and 20 °C/min. The heating rate at 5 °C/ min was shown the starting point. at temperature 264 °C and maximum decomposed rate at 393 °C. The TGA curve of heating rate 10°C/min was provided decomposition at temperature range 288 °C to 374 °C and decomposed temperature range 295 °C to 394 °C for heating rate 20°C/min. (see Figure 4.17-4.19)



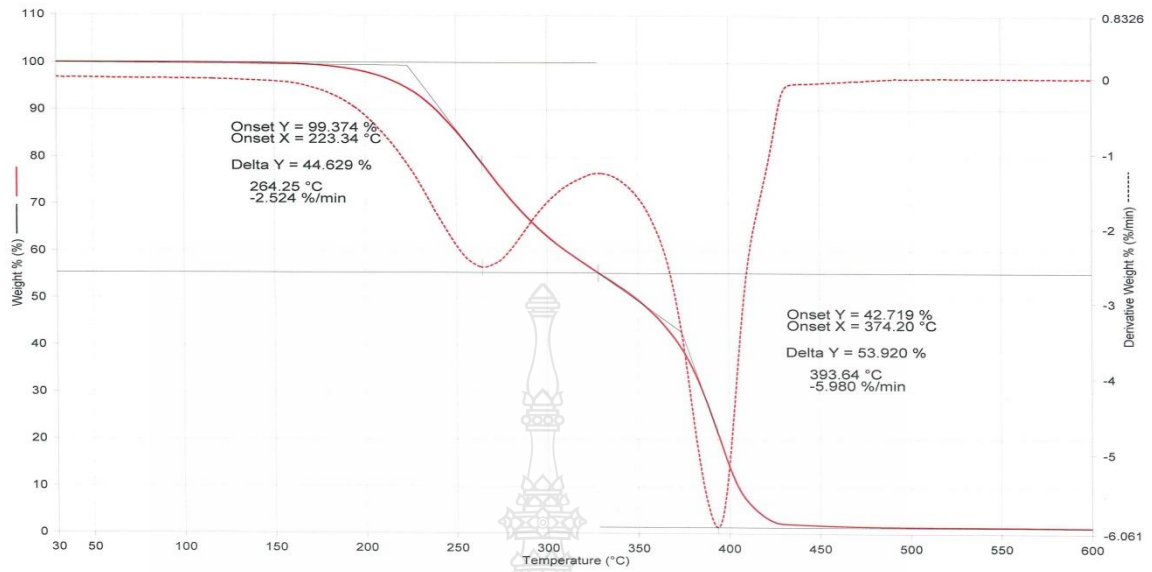


Figure 4.17 TGA curve of Oil:PP at 5°C/min

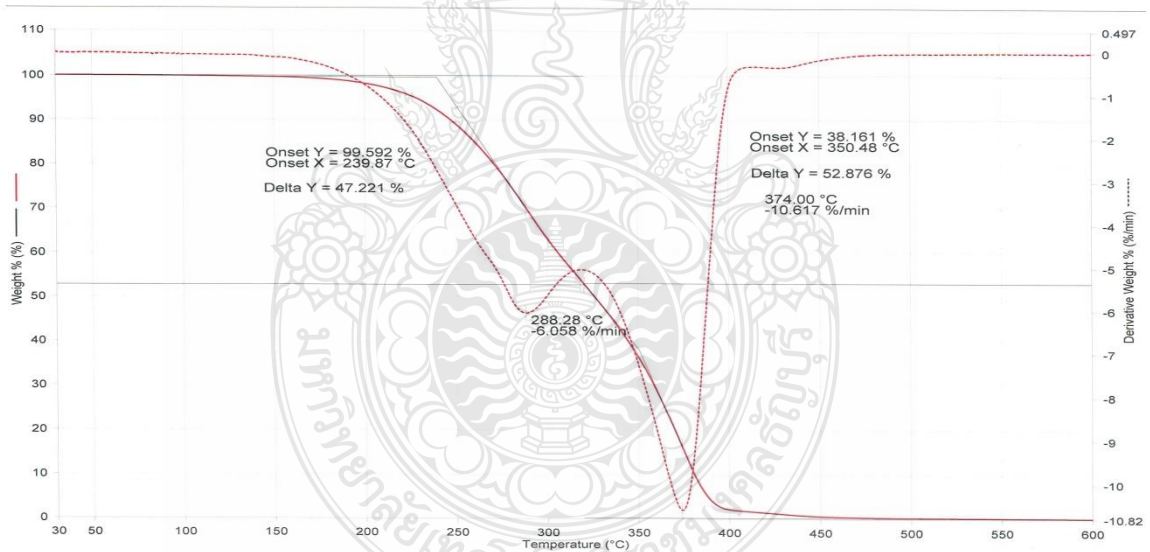
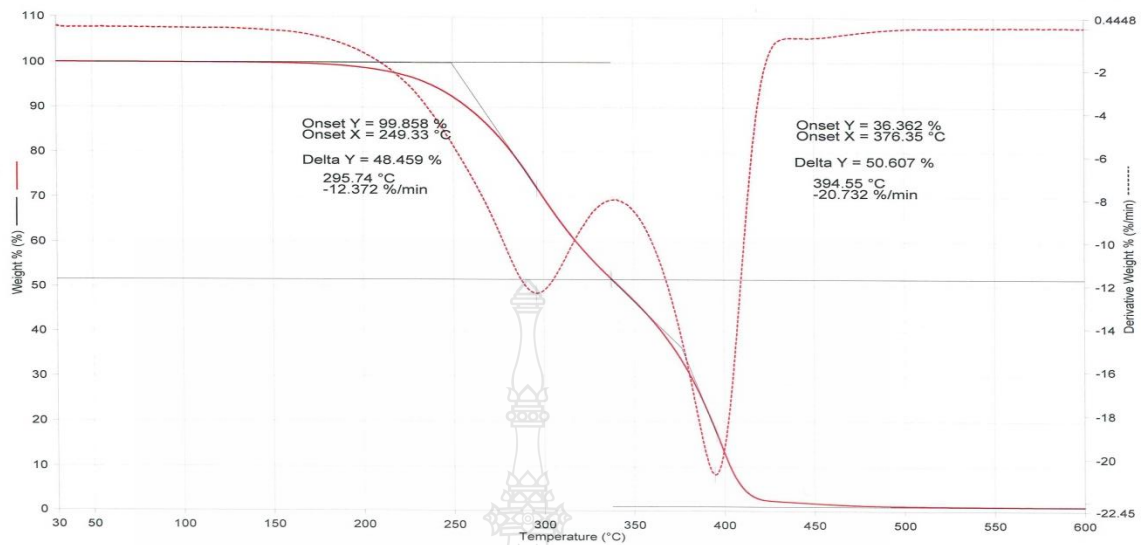


Figure 4.18 TGA curve of Oil:PP at 10°C/min



**Figure 4.19** TGA curve of Oil:PP at 10°C/min

#### 4.6.2 Kinetic of Lubricant oil and high density of polyethylene

From TGA analysis curve of used lubricant oil blending with a high density of polyethylene at heating rate of 5, 10 and 20 °C/min. The heating rate at 5 °C/ min was shown the starting point. at temperature 269 °C and maximum decomposed rate at 444 °C. The TGA curve of heating rate 10°C/min was provided decomposition at temperature range 284 °C to 454 °C and decomposed temperature range 293 °C to 455 °C for heating rate 20°C/min. (see Fig. 4.20-4.22)

#### 4.6.3 Kinetic of Lubricant oil and polystyrene

From TGA analysis curve of used lubricant oil blending with polystyrene at heating rate of 5, 10 and 20 °C/min. The heating rate at 5 °C/ min was shown the starting point. at temperature 274°C and maximum decomposed rate at 413 °C. The TGA curve of heating rate 10°C/min was provided decomposition at temperature range 262 °C to 404 °C and decomposed temperature range 277 °C to 420°C for heating rate 20°C/min. (see Fig. 4.23-4.25)

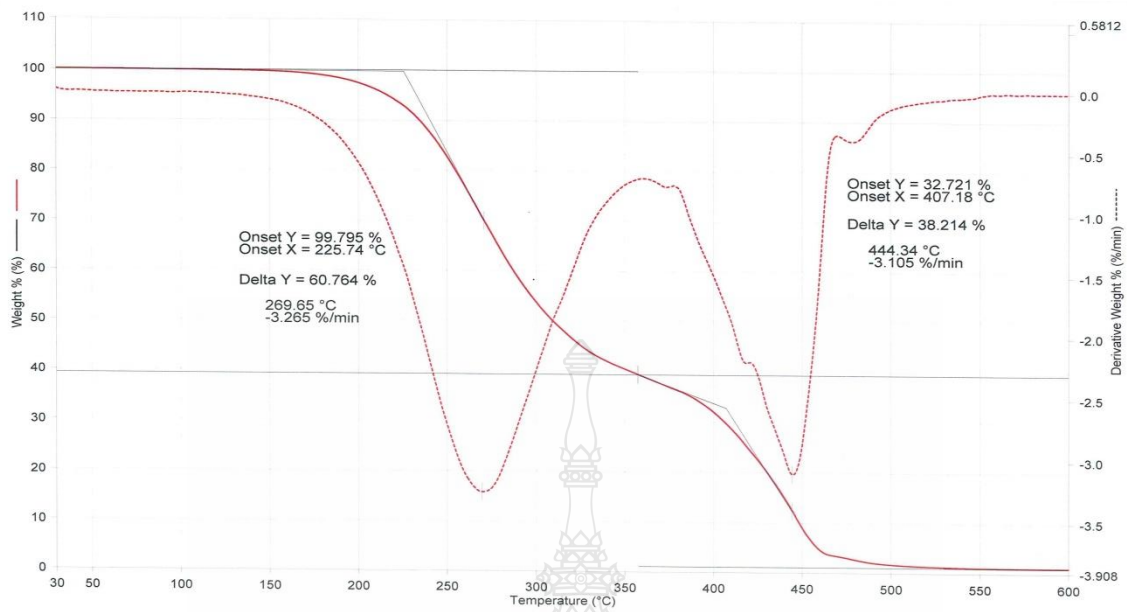


Figure 4.20 TGA curve of Oil:HDPE for heating rate 5 °C/min

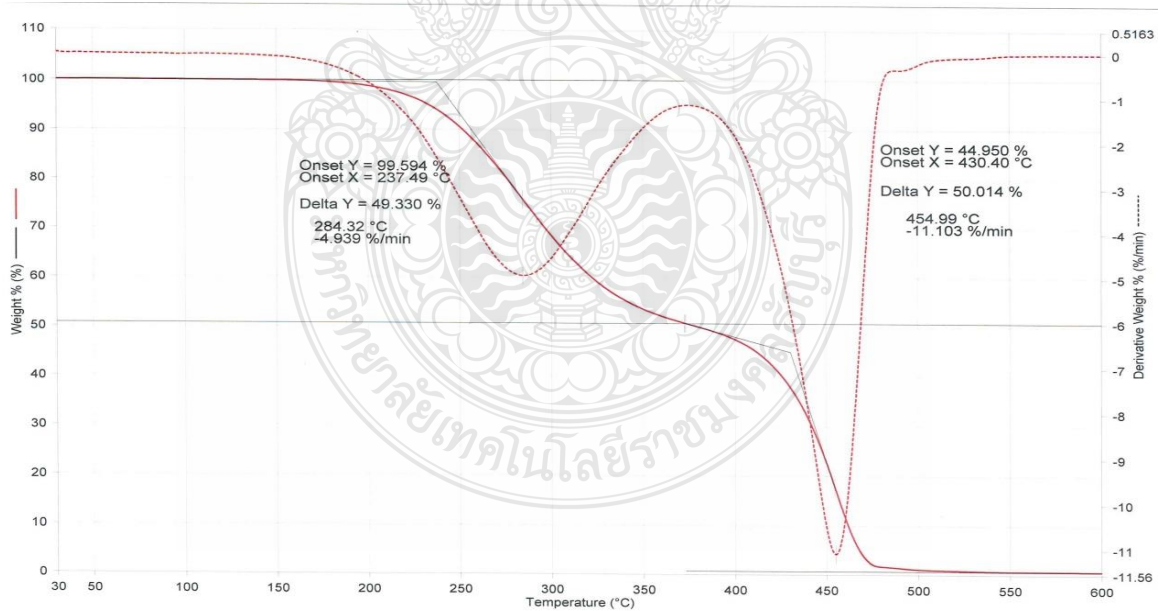
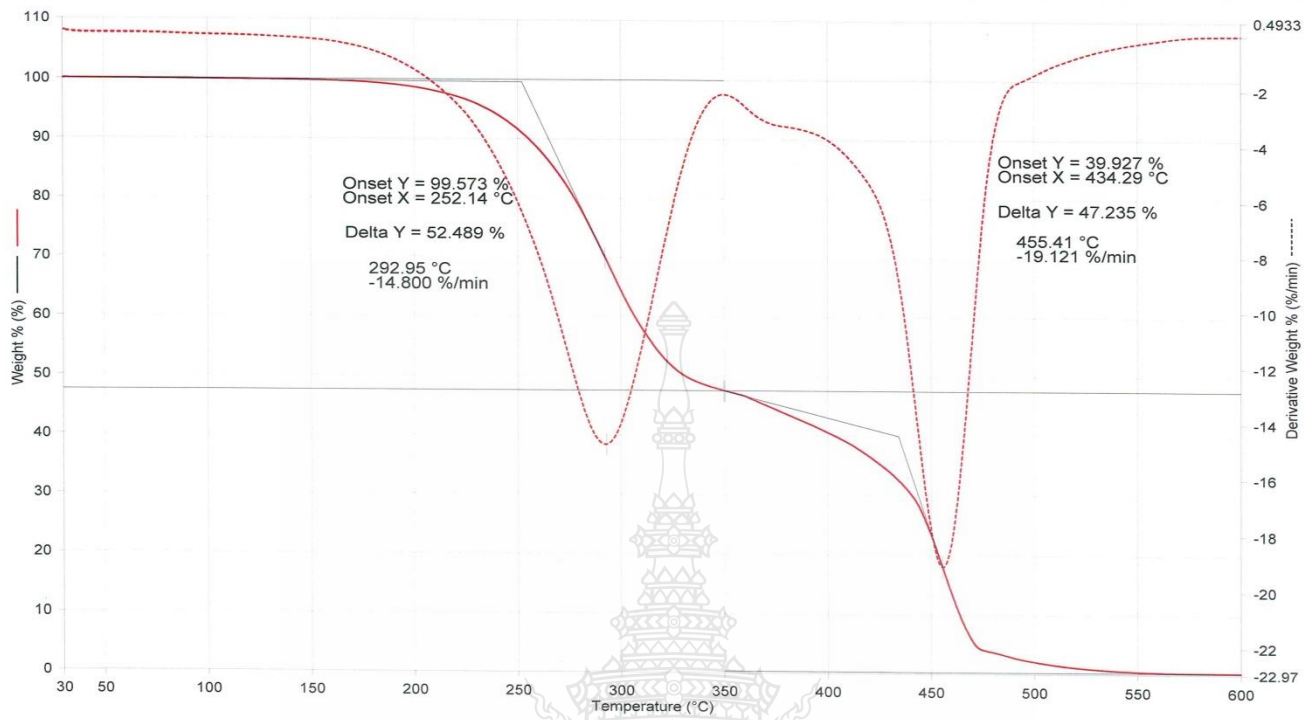


Figure 4.21 TGA curve of Oil:HDPE for heating rate 10°C/min





**Figure 4.22** TGA curve of Oil:HDPE for heating rate 20°C/min



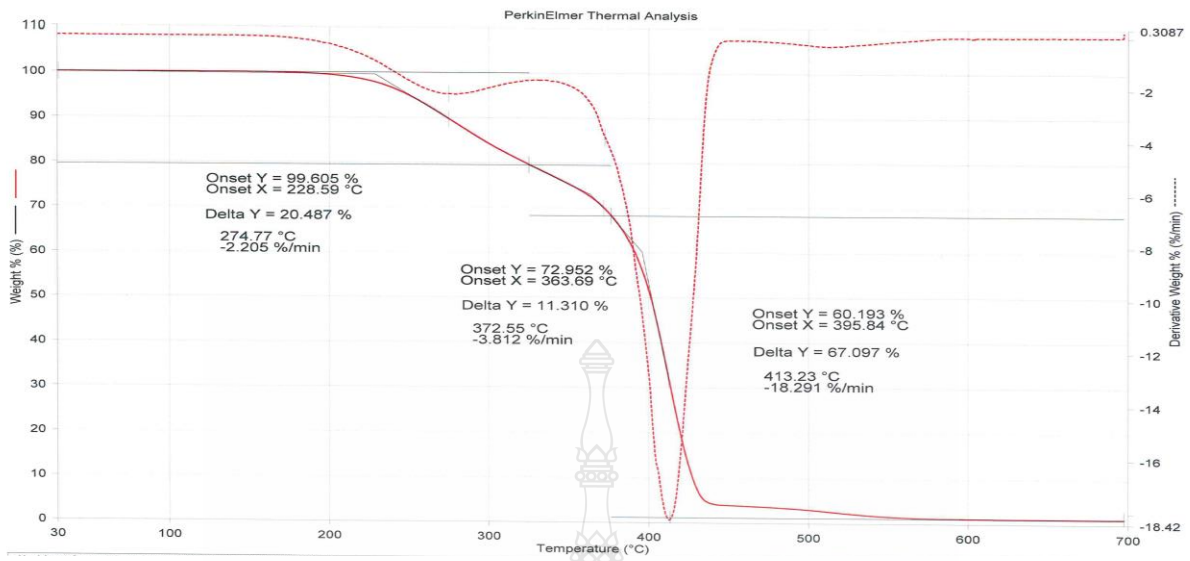


Figure 4.23 TGA curve of Oil:PS for heating rate 5 °C/min

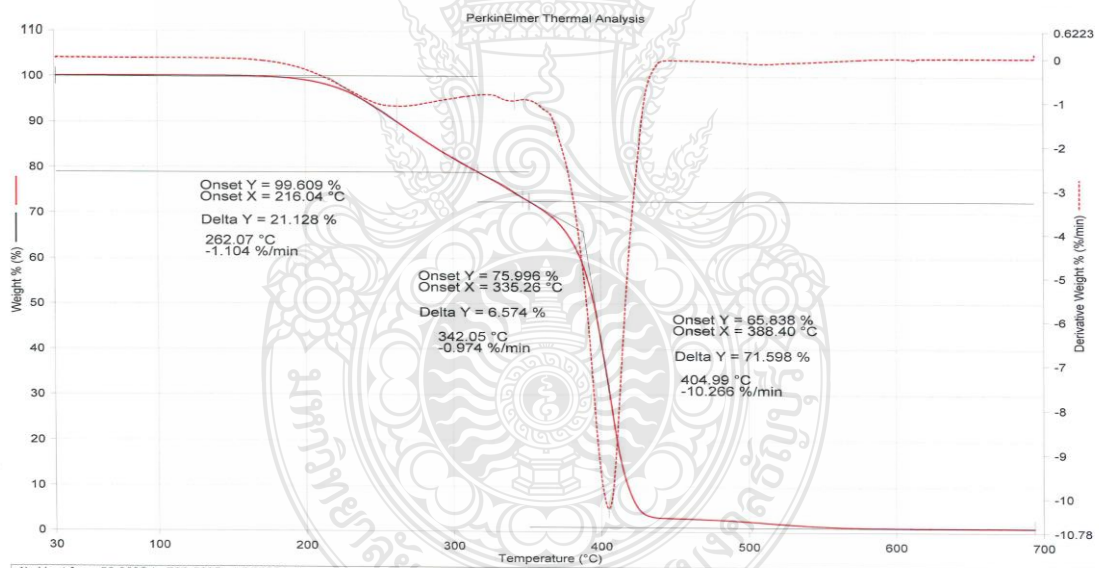
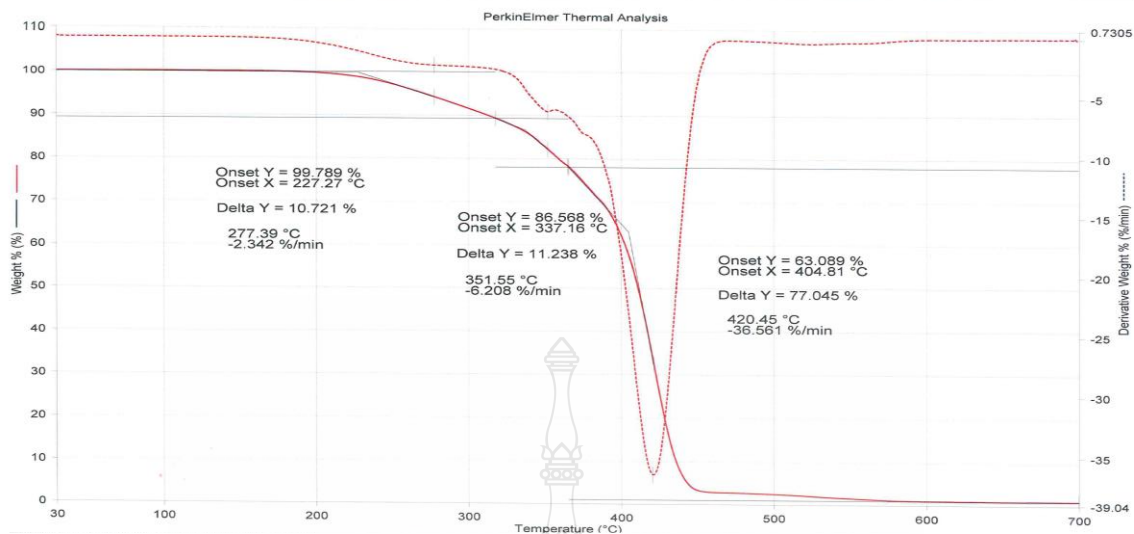


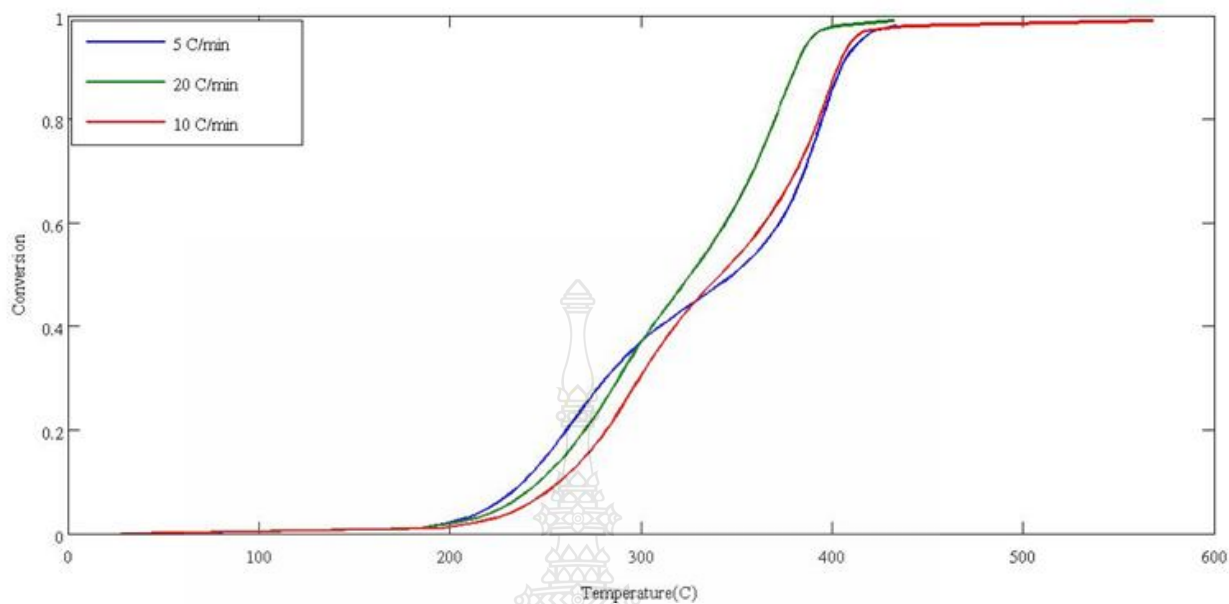
Figure 4.24 TGA curve of Oil:PS for heating rate 10°C/min



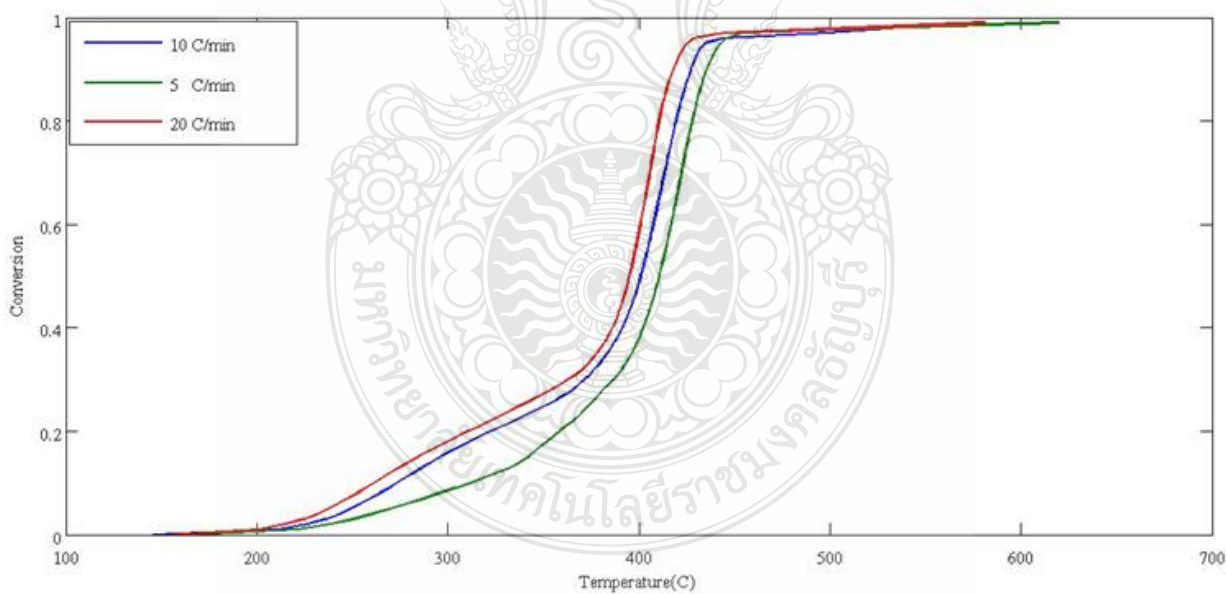
**Figure 4.25** TGA curve of Oil:PS for heating rate 20°C/min

#### 4.6.4 Co-pyrolysis kinetic parameters

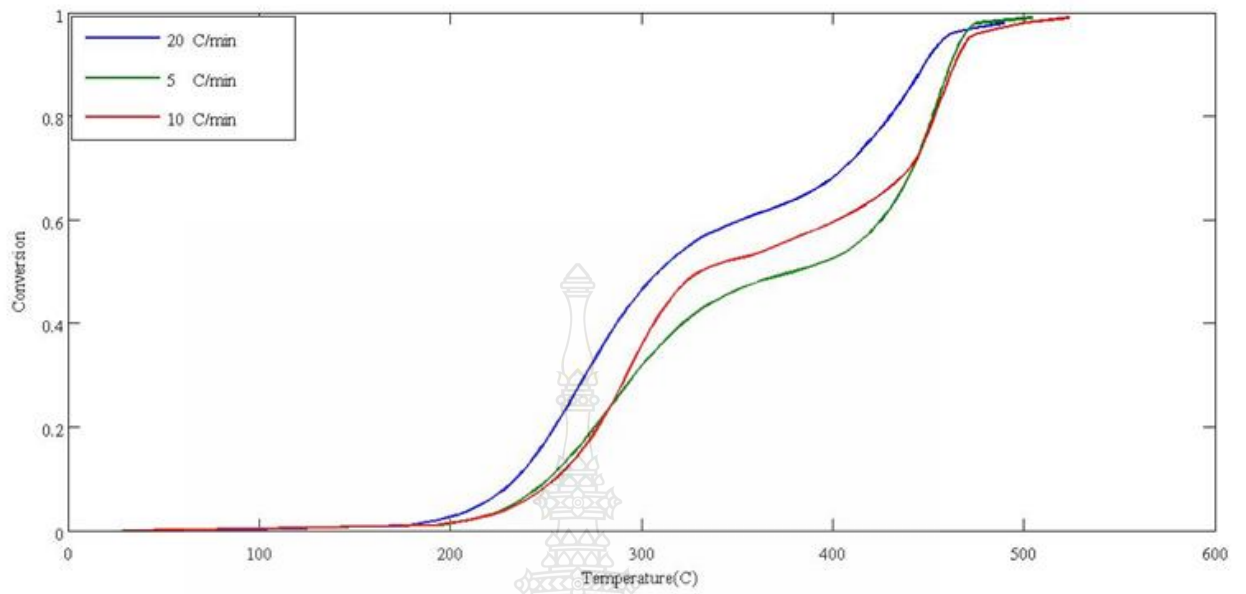
The kinetic parameters of co-pyrolysis for Oil:HDPE, Oil:PP and Oil:PS as shown in Fig. 4.26-4.28, relation between conversion and temperature that occur in TGA by using difference heating rate. The heating rate were found that effect with slope of each curve, increasing heating rate can be increasing the slope.



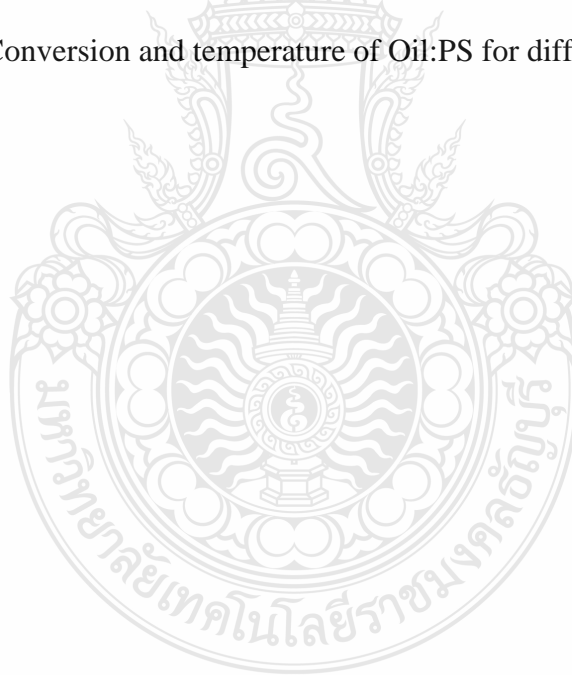
**Figure 4.26** Conversion and temperature of Oil:PP for difference heating rate

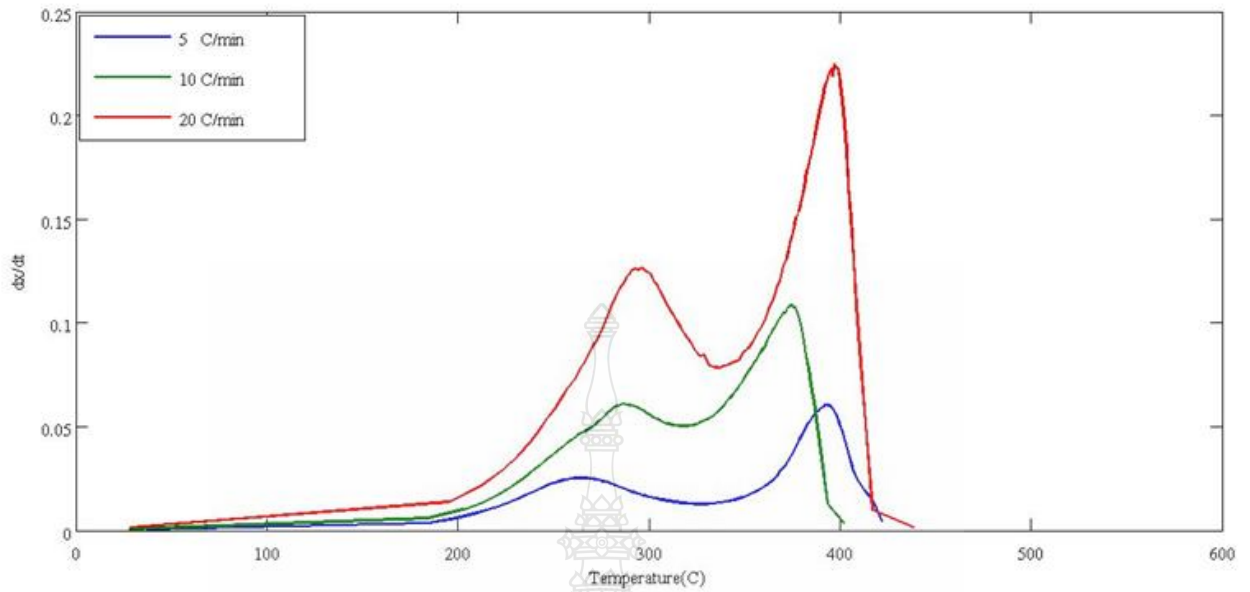


**Figure 4.27** Conversion and temperature of Oil:HDPE for difference heating rate

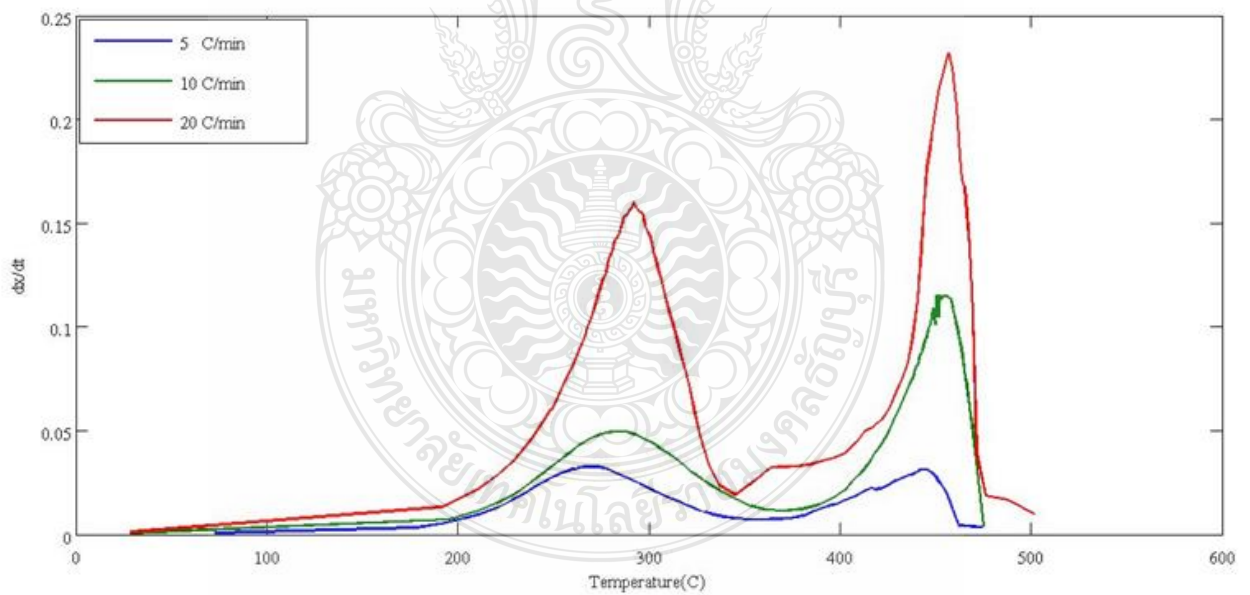


**Figure 4.28** Conversion and temperature of Oil:PS for difference heating rate

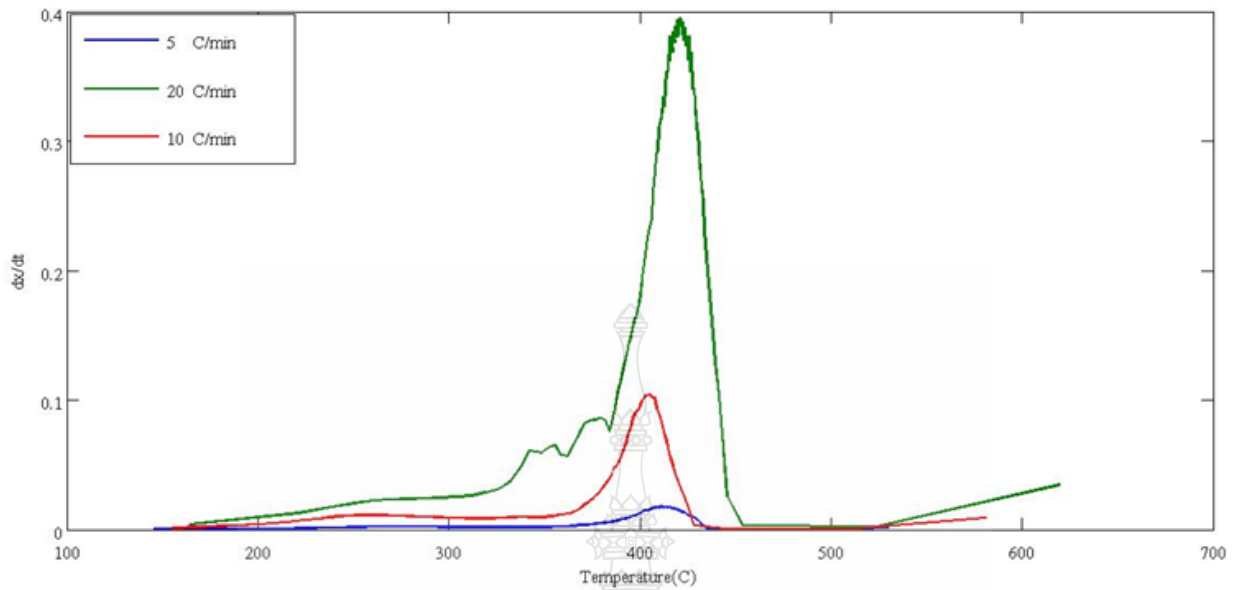




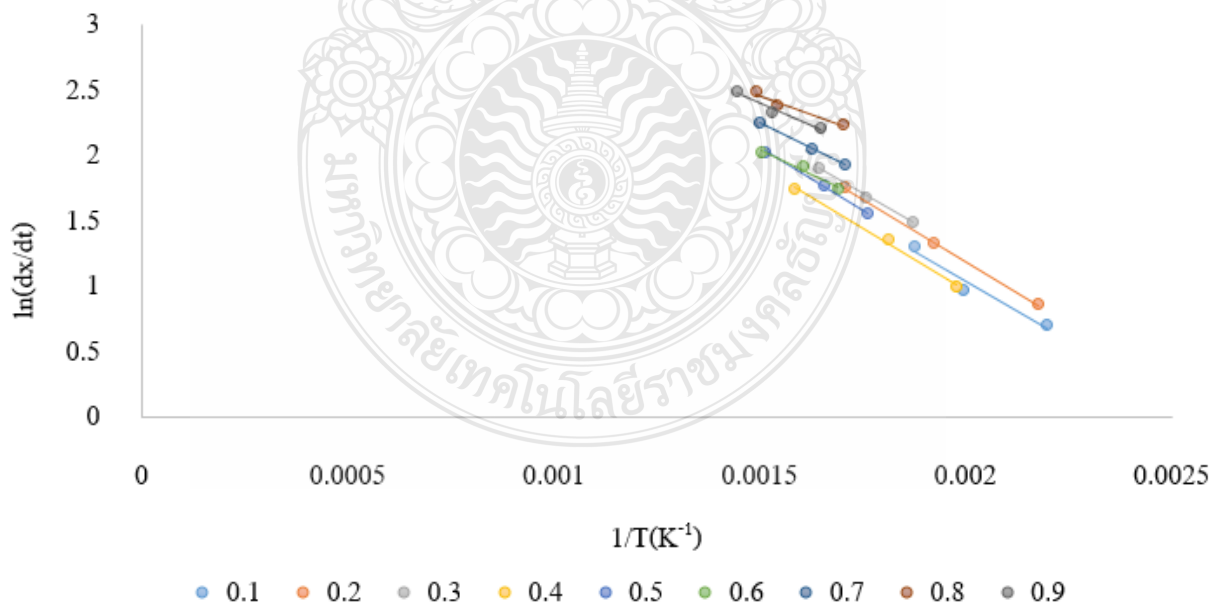
**Figure 4.29** Relationship between  $dx/dt$  and Temperature for difference heating rate of Oil:PP



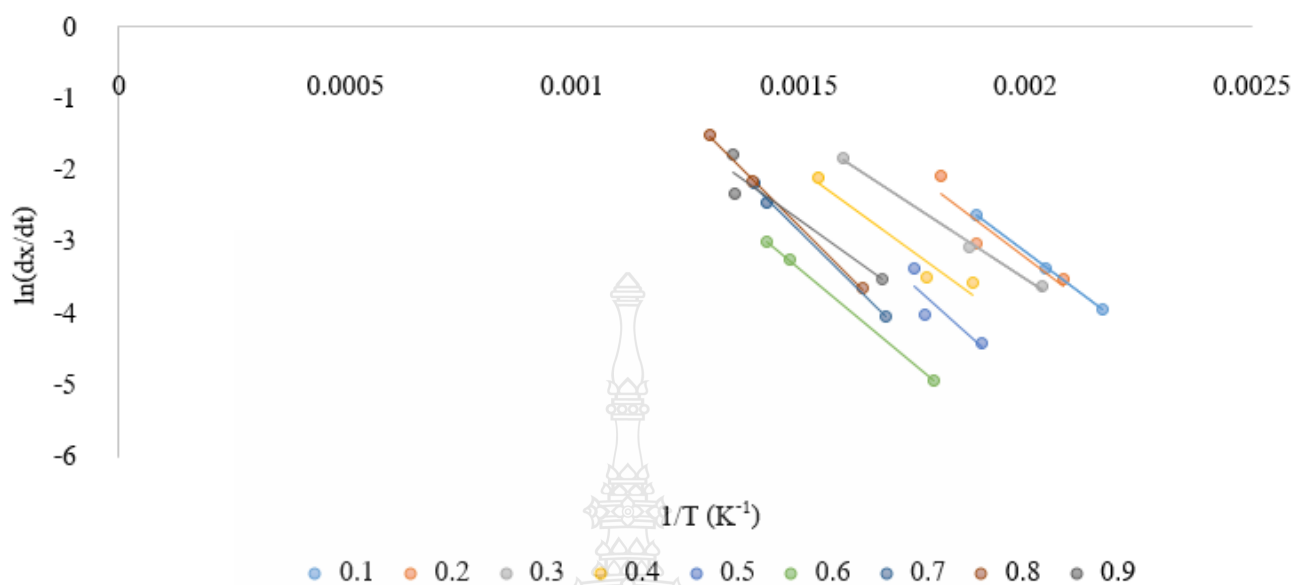
**Figure 4.30** Relationship between  $dx/dt$  and Temperature for difference heating rate of Oil:HDPE



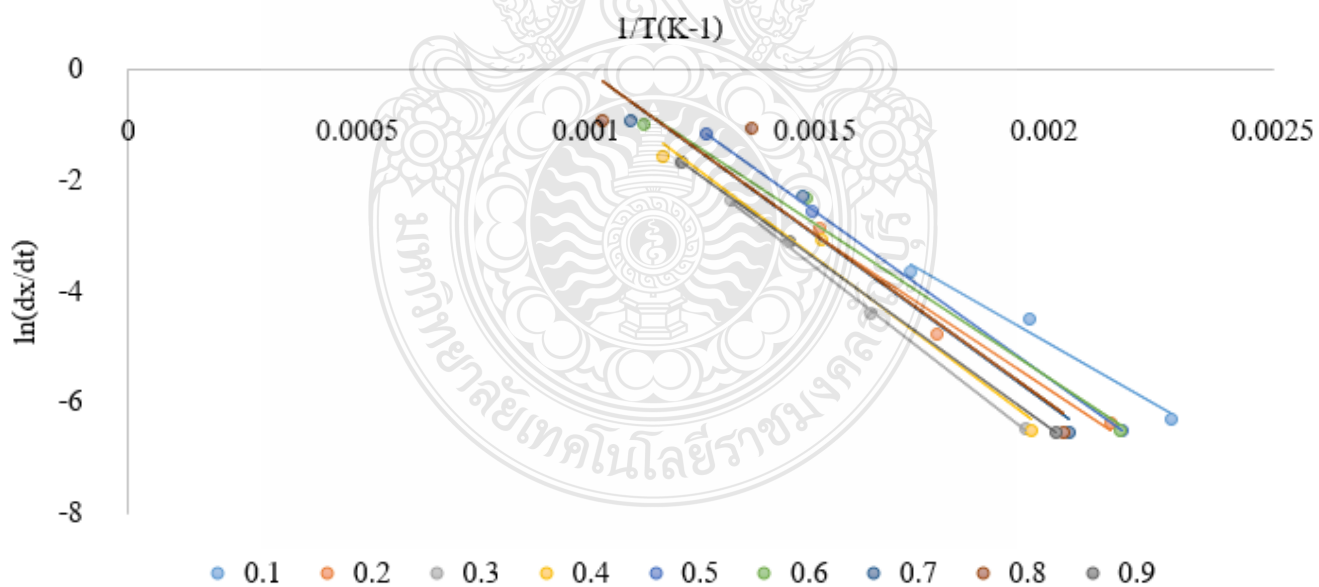
**Figure 4.31** Relationship between  $dx/dt$  and Temperature for difference heating rate of Oil:PS



**Figure 4.32** Relationship of  $\ln \frac{dx}{dt}$  and  $\frac{1}{T}$  for conversion between 0.1-0.9 of Oil:PP



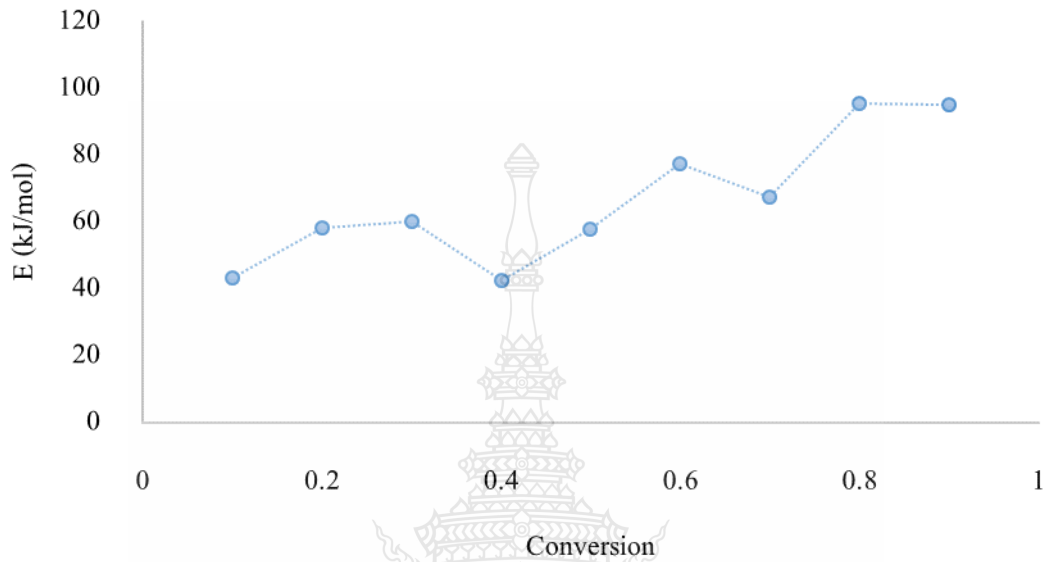
**Figure 4.33** Relationship of  $\ln \frac{dx}{dt}$  and  $\frac{1}{T}$  for conversion between 0.1-0.9 of Oil:HDPE



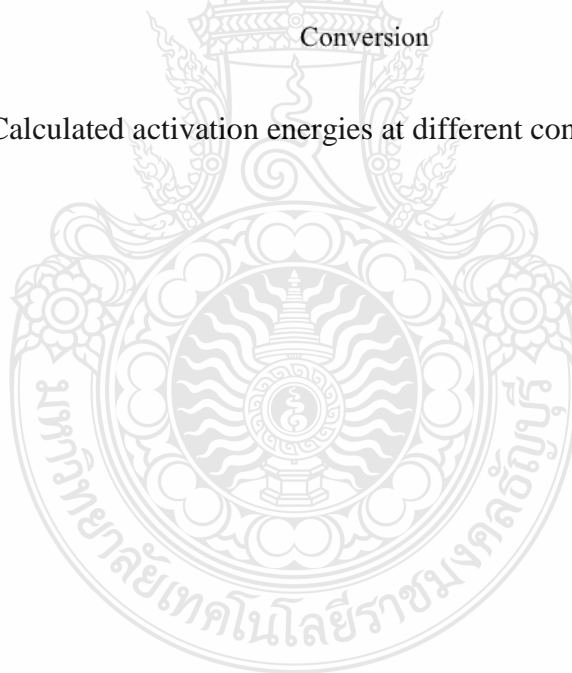
**Figure 4.34** Relationship of  $\ln \frac{dx}{dt}$  and  $\frac{1}{T}$  for conversion between 0.1-0.9 of Oil:PS

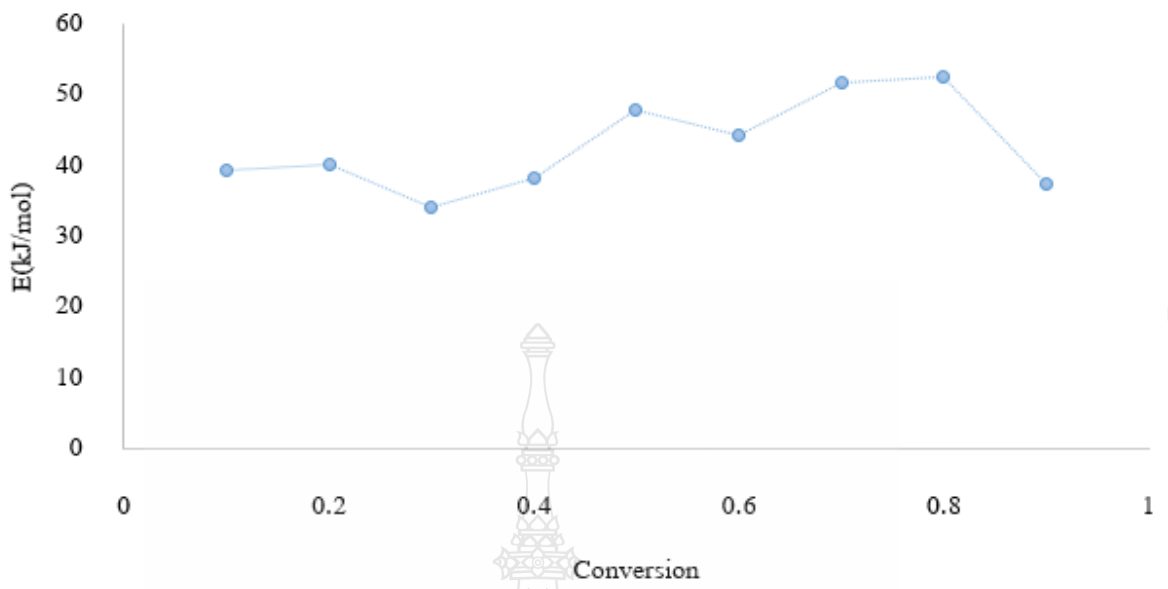


The time with activation energy of each co-pyrolysis. Oil:PP provide activation energy between 9–17.6 kJ/mol<sup>-1</sup> , Oil:HDPE provide activation energy between 34.19 -52.17 kJ/mol<sup>-1</sup> and Oil:PS provide activation energy between 47.22 - 62.22 kJ/mol<sup>-1</sup>

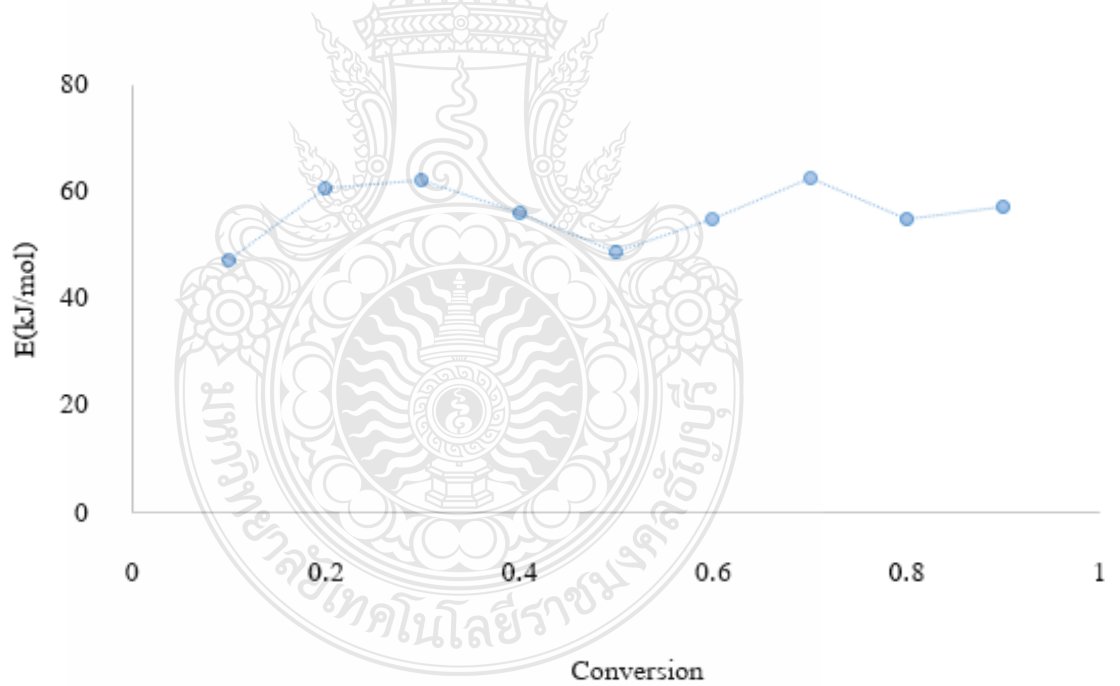


**Figure 4.35** Calculated activation energies at different conversion for Oil:PP





**Figure 4.36** Calculated activation energies at different conversion for Oil:HDPE

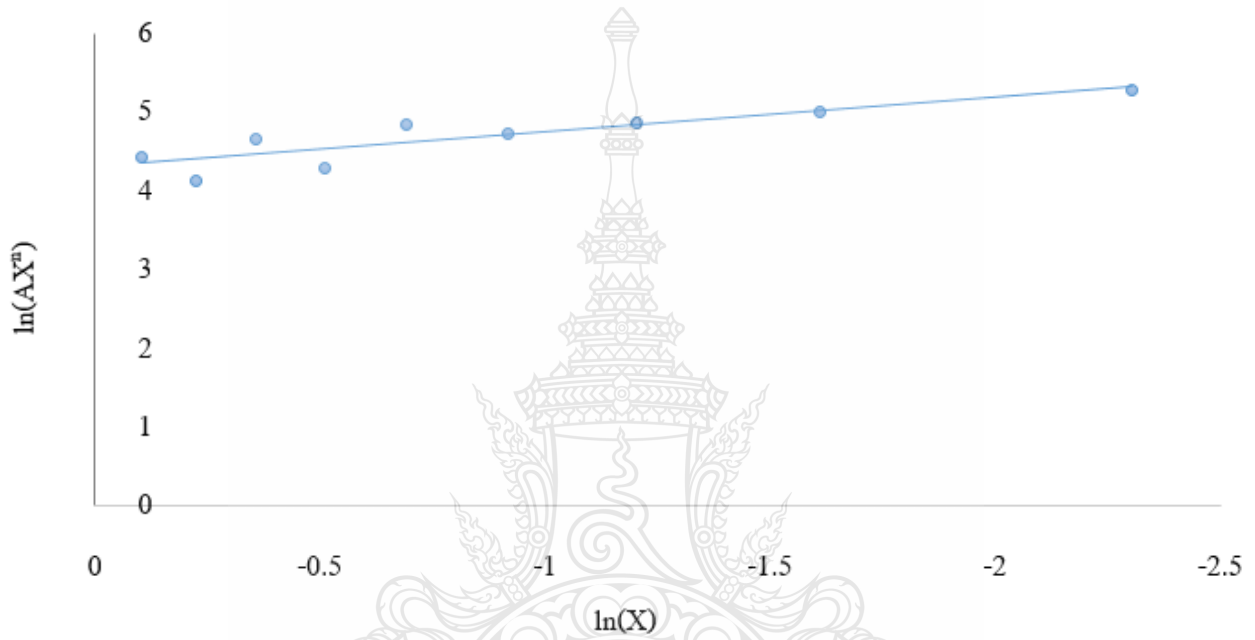


**Figure 4.37** Calculated activation energies at different conversion for Oil:PS

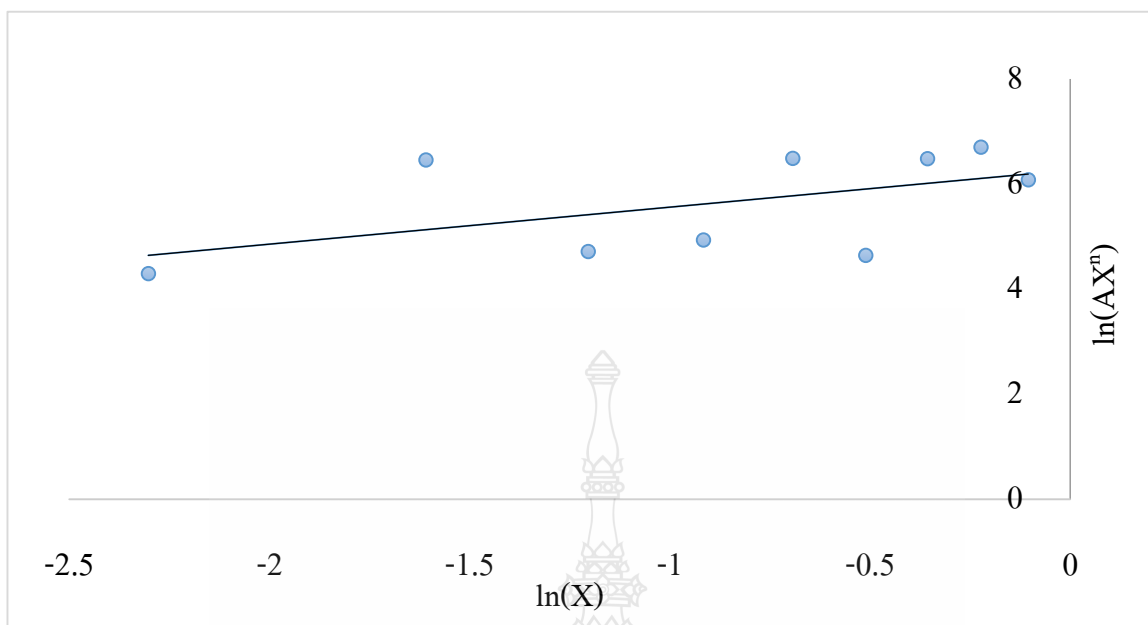
Rearrange Eq. (4.7) for reaction order (n) and activation energy to Eq. (4.8)

$$\frac{dX}{dt} = \frac{-E}{R} \frac{1}{T} + \ln Ax^n \quad (4.8)$$

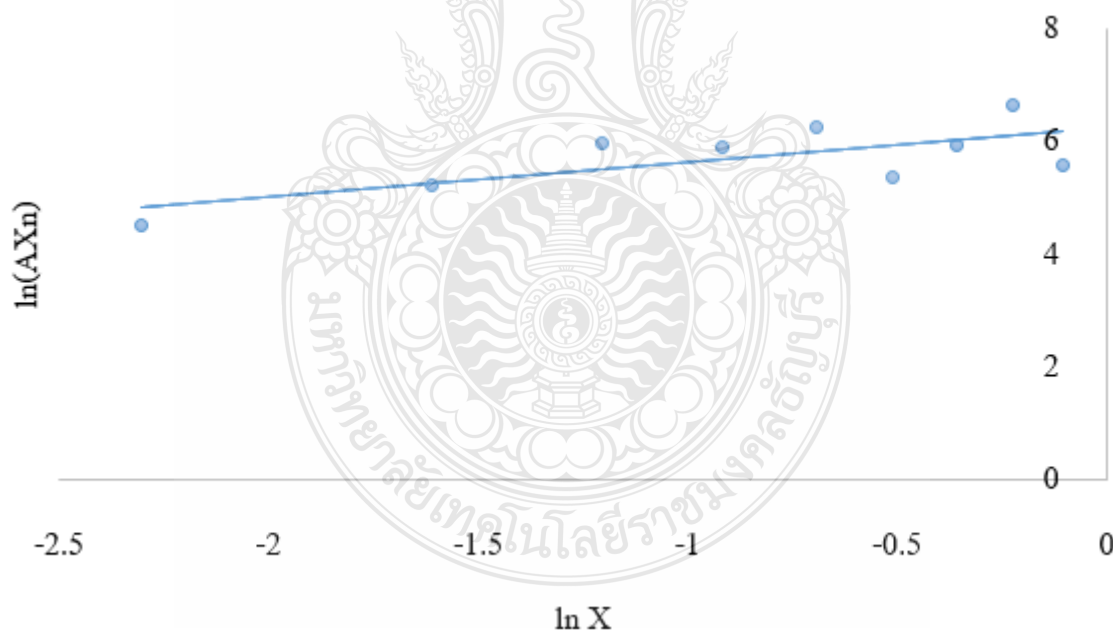
$$\ln Ax^n = \ln Ax^n + n \ln x \quad (4.9)$$



**Figure 4.38** The reaction order for co-pyrolysis of Oil:PP



**Figure 4.39** The reaction order for co-pyrolysis of Oil:HDPE



**Figure 4.40** The reaction order for co-pyrolysis of Oil:PS

**Table 4.12** Kinetic parameters of pyrolysis and co-pyrolysis

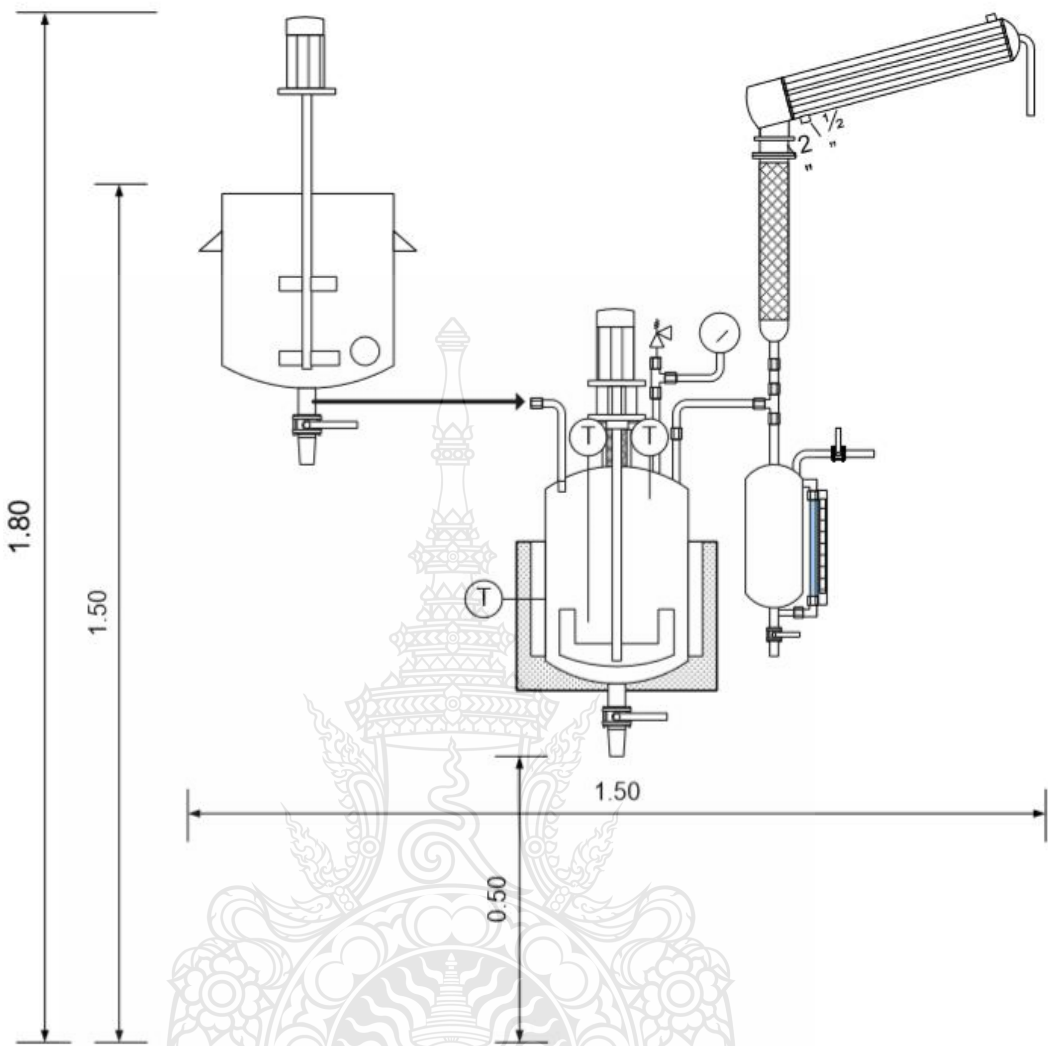
| Materials | Kinetic parameter         |      |        |                             | Ref.       |
|-----------|---------------------------|------|--------|-----------------------------|------------|
|           | k<br>(min <sup>-1</sup> ) | n    | A      | E<br>(kJmol <sup>-1</sup> ) |            |
| Oil:HDPE  | 203.97                    | 0.36 | 206.52 | 52.47-34.19                 | This study |
| Oil:PP    | 73.85                     | 0.44 | 74.15  | 43.08-95.21                 | This study |
| Oil:PS    | 509.66                    | 0.62 | 518.01 | 47.22-62.22                 | This study |
| Oil:PS    |                           | 0.46 | 103.31 | 176-369                     | [44]       |
| Oil       |                           | 1.35 | 334.22 | 282-448                     | [44]       |
| PS        |                           | 0.32 | 60.60  | 164-249                     | [44]       |
| HDPE      |                           |      |        | 238-247                     | [33]       |
| PP        |                           |      |        | 179-188                     | [33]       |

Kinetic tests on the pyrolysis of mixture of waste lubricating oil and three types of plastic waste were carried out using a thermogravimetric analysis technique at the heating rate of 5 °C/min, 10 °C/min and 20 °C/min. The apparent activation energy and the apparent order of reaction were determined at conversion from 1 to 90%. The apparent activation energies increased with increased of conversions. Most of activation energies of co-pyrolysis less than individual waste lubricant oil: Oil>HDPE>PS>PP. The arrange of activation energies of co-pyrolysis are: Oil:HDPE>Oil:PS>Oil:PP. The order reactions of co-pyrolysis reaction were shown order less than 1.0.

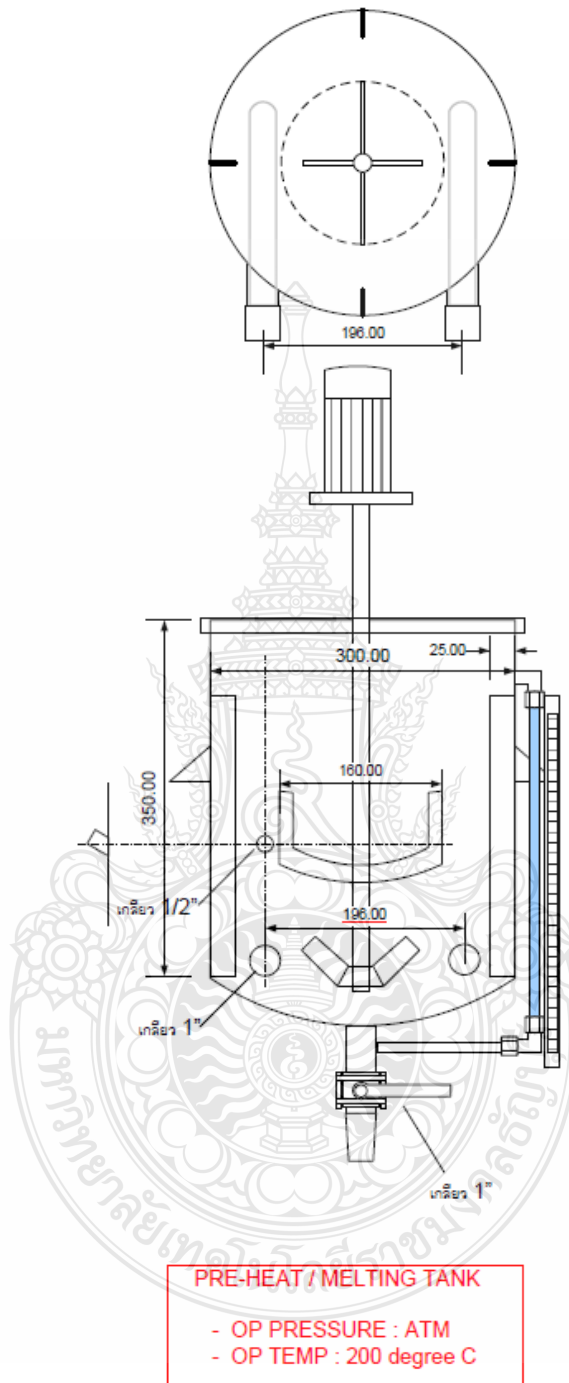
#### 4.7 Scale up and co-pyrolysis design of prototype

Design Concept of co-pyrolysis prototype of used lubricant oil and waste plastic as follow:

- Keep composition of raw materials constant before feed to the reactor – Melting tank
- Reactor temperature reach 450°C – Final temperature in the reactor
- Heating rate and temperature pattern – Heating rate 10°C/min
- Maximum temperature- materials and heater- The overshoot temperature is 600°C
- Maximum pressure in the reactor- Selected safety valve relief at 1.0 bar
- Semi-batch feed- control feed flow rate and can reduced reactor volume.
- Cooling water temperature- type of cooling bath
- Temperature of melting tank- all raw materials is homogenous phase



**Figure 4.41** Dimension of co-pyrolysis prototype



**Figure 4.42** Melting tank drawing

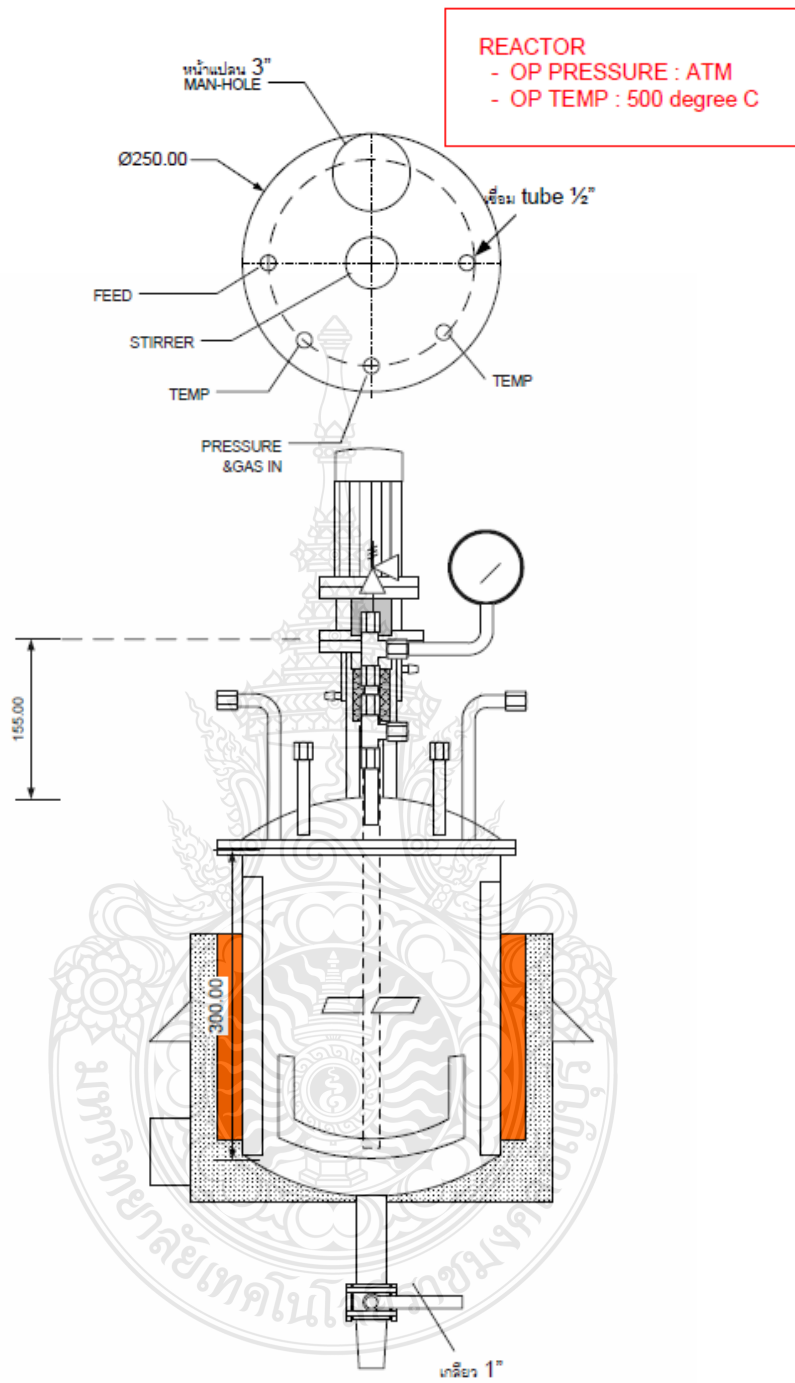
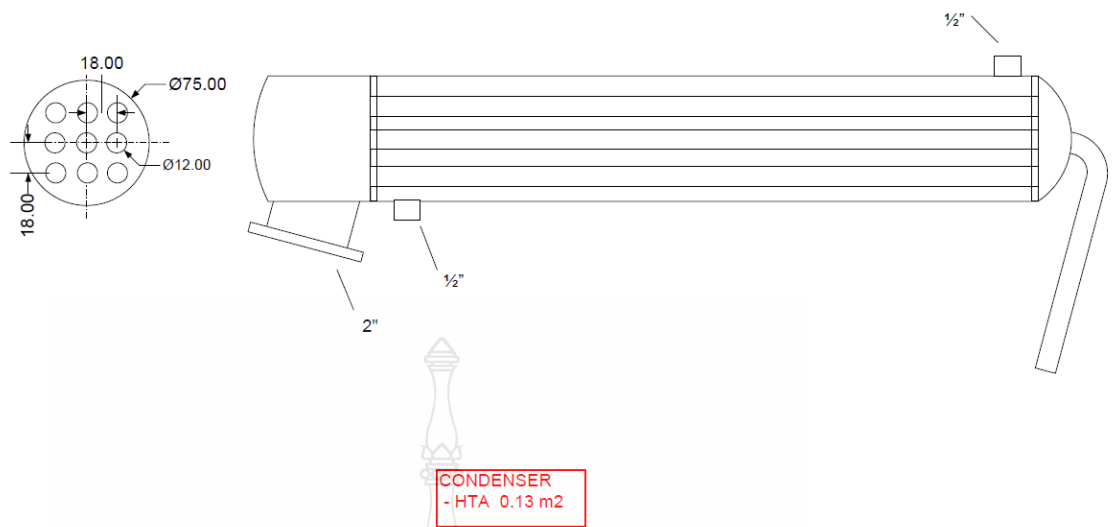
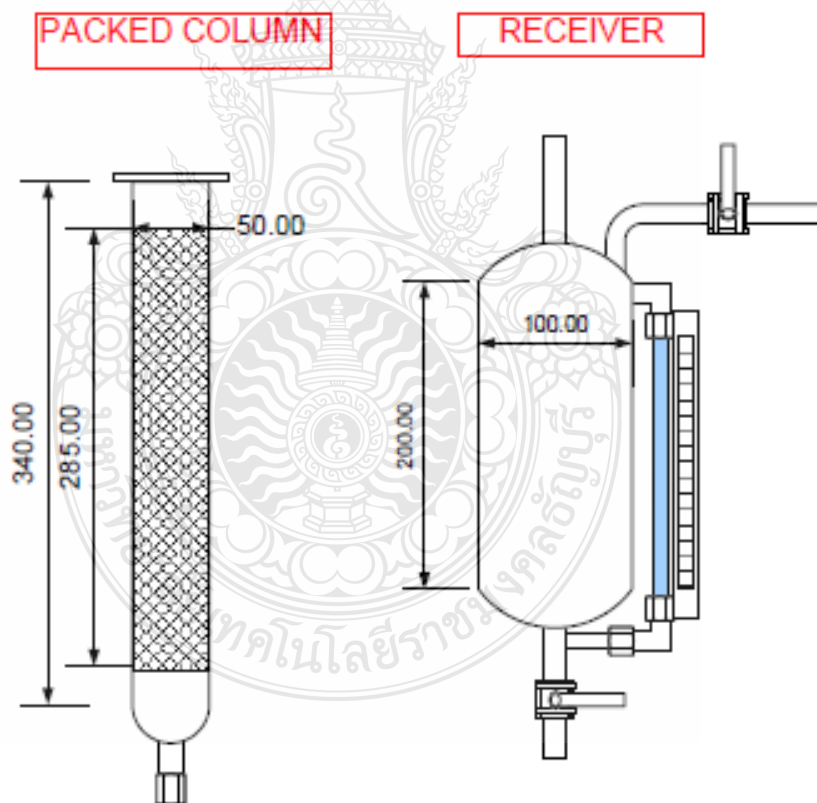


Figure 4.43 Reactor drawing

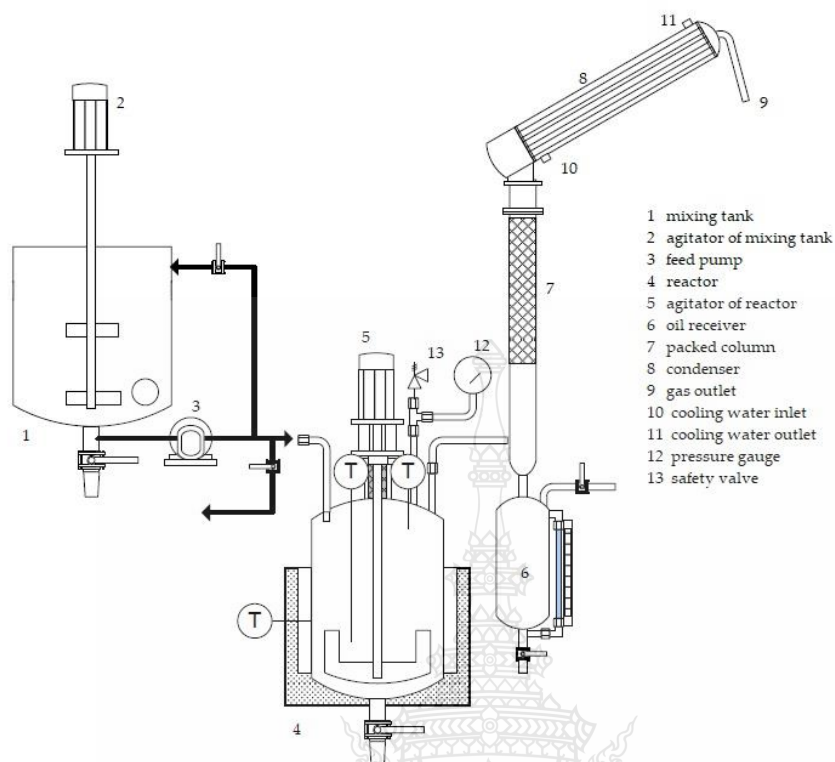




**Figure 4.44** Condenser drawing



**Figure 4.45** Packed column and oil receiver



**Figure 4.46** Co-pyrolysis prototype drawing

The novelty of this research are

- Optimization of proportion of raw materials between used lubricant oil and mixed plastic wastes.
- Pyrolysis oil will focus on the properties of diesel and the range of carbon atoms.
- Design process for controlling the proportion of homogeneous raw materials before entering into a semi-batch reactor at heat cracking temperatures

**Table 4.13** Temperature pattern for controller heater

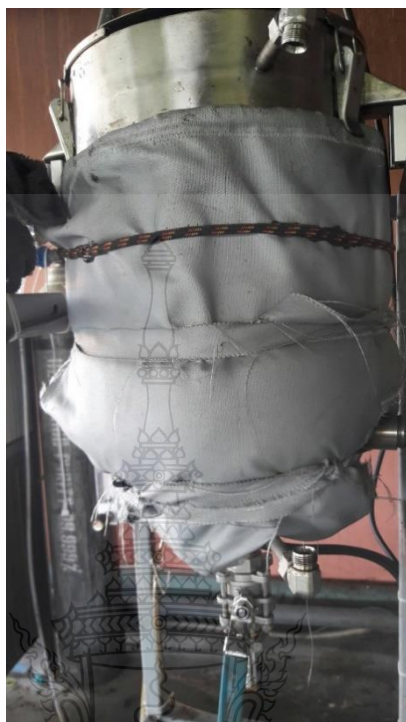
| Set Point Temperature of Jacket (°C) | Lamping Time (min) | Holding time (min) |
|--------------------------------------|--------------------|--------------------|
| 300                                  | 50                 | 10                 |
| 350                                  | 10                 | 10                 |
| 450                                  | 20                 | 30                 |
| 500                                  | 10                 | 30                 |



**Figure 4.47** Too many smogs occur



**Figure 4.47** The heater dip type to clothe type



**Figure 4.48** The heater clothe type



**Figure 4.49** Gear pump shutdown because raw materials rapidly harden.



**Figure 4.50** Proportion 50:30:20:0 (right), 50:30:10:10 (left)

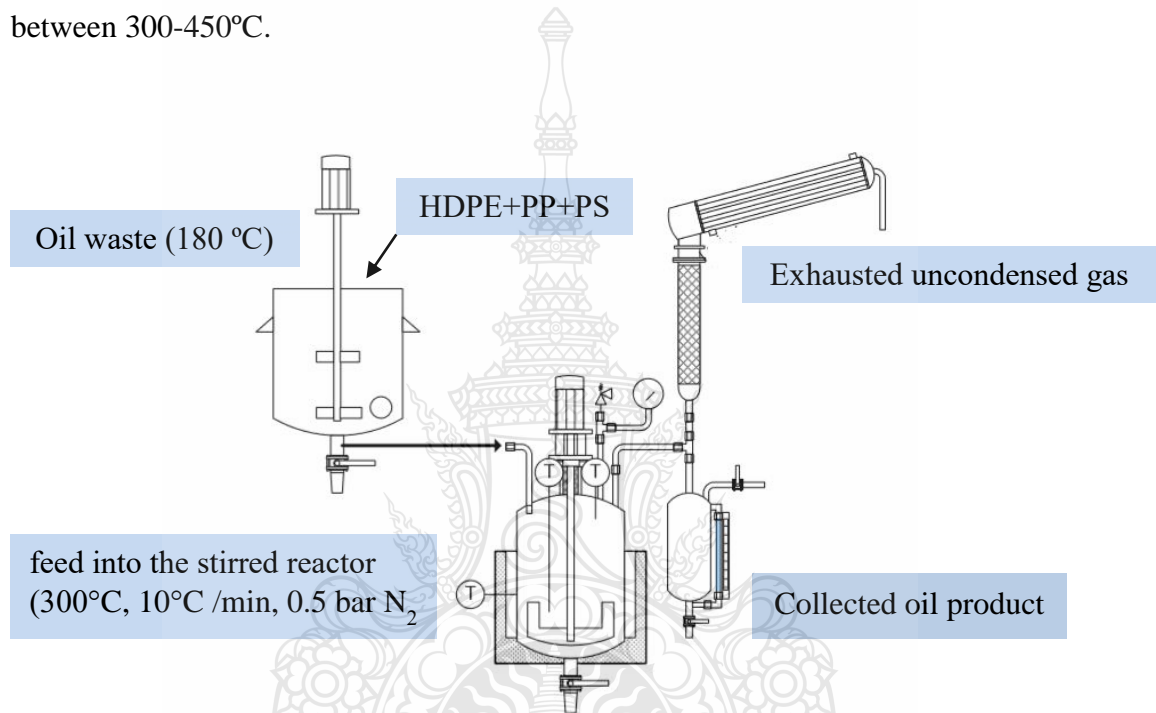
The problem of prototype design such as raw materials rapidly harden, change heater type cause by smog of used lubricant oil in melting tank.



**Figure 4.51** The real co-pyrolysis prototype

#### 4.8 Co-pyrolysis of prototype

The optimum proportion of co-pyrolysis was selected from laboratory, Oil:HDPE:PP:PS as 50:30:20:0. Firstly, 1<sup>st</sup> tank is dehydration of used oil (110°C for an hour) and then melted all raw materials in the melting tank at 180°C for 1 hr. and then feed into the reactor at 300 °C (heating rate 10 °C/min). Pressure in the reactor was controlled by manual, keep it near 0.5 bar gauge. Thermal cracking reaction occur between 300-450°C.

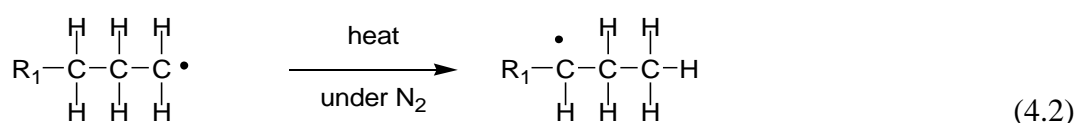
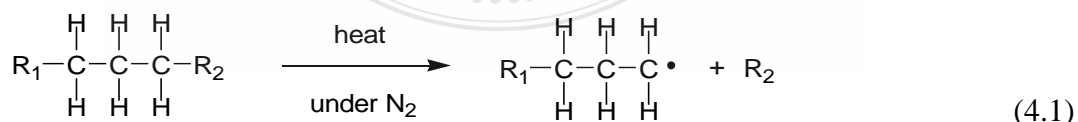


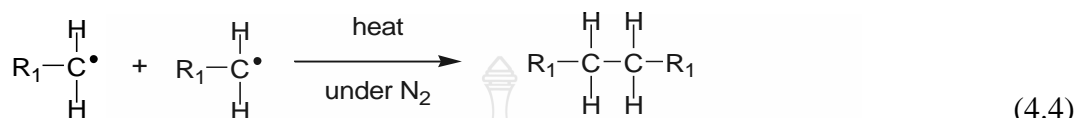
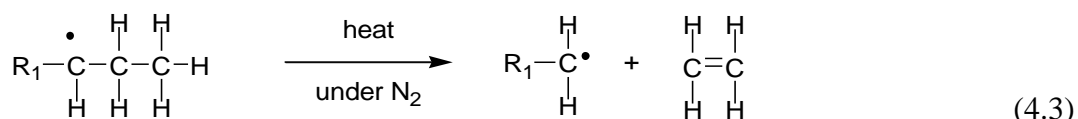
**Figure 4.52** Co-pyrolysis prototype detail of operation

**Table 4.14** Properties of the pyrolytic oil from the prototype (10 kg/day).

| Properties                     | Prototype  |            |            | Lab-Scale | Standard of Diesel |
|--------------------------------|------------|------------|------------|-----------|--------------------|
|                                | 300–400 °C | 400–425 °C | 425–450 °C |           |                    |
| Flash point (°C)               | 29         | 35         | 37         | 29        | >52                |
| Viscosity (cSt) @ 40 °C        | 2.02       | 3.71       | 5.84       | 1.98      | 1.8–4.1            |
| Specific gravity               | 0.81       | 0.82       | 0.82       | 0.81      | 0.81–0.87          |
| Distillation °C @ 90% recovery | 299        | 347        | 373        | 353       | <357               |
| Colour                         | 3.5        | 4.0        | 4.5        | 2.5       | <4.0               |
| Cetane index                   | 53         | 66         | 67         | 65        | >50                |

The comparison between oil product properties from the lab-scale shown in Tables 4.14, oil from prototype at temperature range 400–425°C showed improved properties better than lab scale properties, increasing of flash point, viscosity, specific gravity and cetane index. The comparison of product yields between laboratory and prototype showed in Table 4.15, the prototype process provided the total oil yields of 68.86%. Most of oil yields were produced at the temperature range of 400–425°C (31.64%) along with temperature range 425–450°C (22.87%), and 300–400 °C (14.35). The total oil yield and solid yield (68.86% and 23.72%) of the prototype process were higher than the lab-scale oil and solid yields (63.36% and 18.42%, respectively) however, solid yield of prototype that higher than lab-scale cause by reacted in short time (80 minute). The higher oil yields may be due to higher heat transfer because of stirred in the larger volume of the prototype reactor which could accelerate C-C bond cracking. This research propose a mechanism for the pyrolysis of long chain hydrocarbons as shown in Equations (4.1)–(4.4):





**Table 4.15** Pyrolysis products yields for different temperature range (Prototype).

| Products      | Yield (%wt.) |            |            | Lab Scale  |
|---------------|--------------|------------|------------|------------|
|               | 300–400 °C   | 400–425 °C | 425–450 °C | 300–450 °C |
| Oil           | 14.35        | 31.64      | 22.87      | 63.36      |
| Solid residue |              | 23.72      |            | 18.42      |
| Gas           |              | 7.42       |            | 18.22      |
| Total         |              | 100.00     |            | 100.00     |

The first reaction in the mechanism is to start by cracking the heat of the CC bond to produce the main carbon free radical in the product (equation (4.1)), followed by isomerization and more stable free radicals (Equation (4.2)). Then, the breakdown of C-free radicals and C bonds in the equation (4.3) causes free radicals from carbon that are shorter in the chain length and alkene compounds, followed by a combination of two free radicals to create Small alkane molecules (Equation (4.4)) [38]

The composition of the raw material and the prototype design affects the increase in oil content and the decrease in the amount of gas due to the raw materials entered into the reactor within the same range.

Pressure and flow rate of the carrier gas are important parameters for increasing productivity and product composition. [15]. Therefore, compared with the working



conditions used in the laboratory and the higher pressure prototype pyramid (0.5 bar gauge) and the flow of nitrogen through the reactor helps improve the composition of oil products at the prototype level. Nitrogen gas is often used in the pyrolysis process and produces oils that contain high olefins and paraffin [39,40].



## CHAPTER 5

### CONCLUSION

#### 5.1 Conclusion

Co-pyrolysis between used lubricant oil and each type of waste plastics, proportion of Oil:HDPE, Oil:PS and, Oil:PP were studied, optimum ratio of each blending were 50:50, 50:50, and 75:25, respectively. Blending of Oil:HDPE and Oil:PS were produced pyrolytic oil that had five properties (flash point, viscosity, specific gravity, color and distillation) on the diesel standard. Proportion 75:25 of Oil:PP was found only flash point lower than diesel standard.

The analytical component of hydrocarbon by GC-MS of co-pyrolysis oil, linear paraffins  $<C_{24}$ , were increased when amount of used lubricant oil increased. Most oil products had high quantity of linear paraffins  $<C_{24}$  (Oil>HDPE>PP>PS) and subsequent by hydrocarbon compound with double bonds (HDPE>PP>PS>Oil).

The co-pyrolysis of waste oil blended with one, two, and three types of plastic waste were carried out under nitrogen gas at atmospheric pressure on a lab-scale. The optimised proportion of raw materials selected was 50:30:20:0 % wt. (Oil:HDPE:PP:PS) by considering the properties of the oil products such as flash point, distillation value, color, viscosity, specific gravity and cetane index. The proportion of raw materials that produce oil products that meet the standard criteria for diesel fuel that the Ministry of Energy of Thailand has been selected for further study using the prototype scale system. Based on the analysis of oil products from GC-MS, it was found that Co-pyrolysis of waste oil mixed with non-polystyrene plastic waste showed high paraffin (55.723%) and 35.363% olefins. The summary of the hydrocarbon liner is 91.086%. The number of carbon atoms in the composition of most oil products is in the diesel range (45.28%) corresponding to the properties of diesel products that pass the standard of diesel.

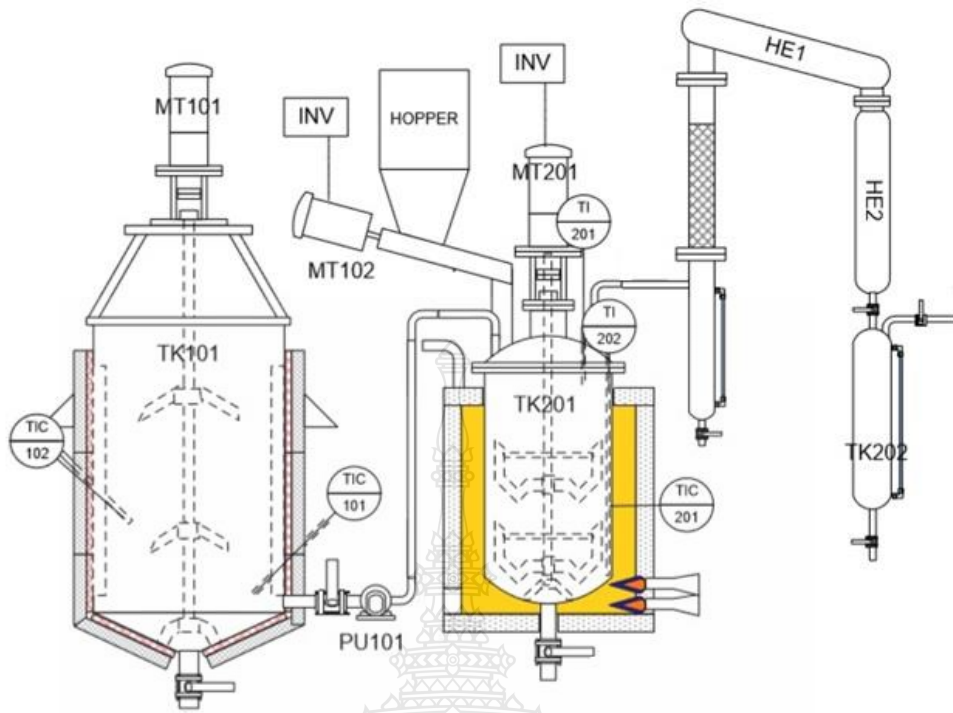
The heat transfer limitation of plastic waste in the pyrolysis process affects the design of the reactor, requiring high agitation of mixing results in increasing the heat transfer potential of co-pyrolysis, plastic lubricant. The waste is a simple design of a reactor, a batch reactor with turbulence, low speed and low construction costs. The prototype pyrolysis process consists of two steps: first, the raw material that dissolves in the

homogeneous phase and the second step is thermal cracking in the reactor at the decomposition temperature (300°C). Therefore, the co-pyrolysis prototype has good performance, produces fuel like diesel that produces higher yield (68.86% wt.) than the laboratory level (63.36% wt.), received lower gas yield due to pressure higher (0.5 bar pressure gauge) The flow of nitrogen through the stirring reactor and the raw material enters the homogeneous phase from the melting tank. The novelty of this work are optimization of proportion of used lubricant oil and mixed plastic wastes and focused on which proportion provide diesel properties.

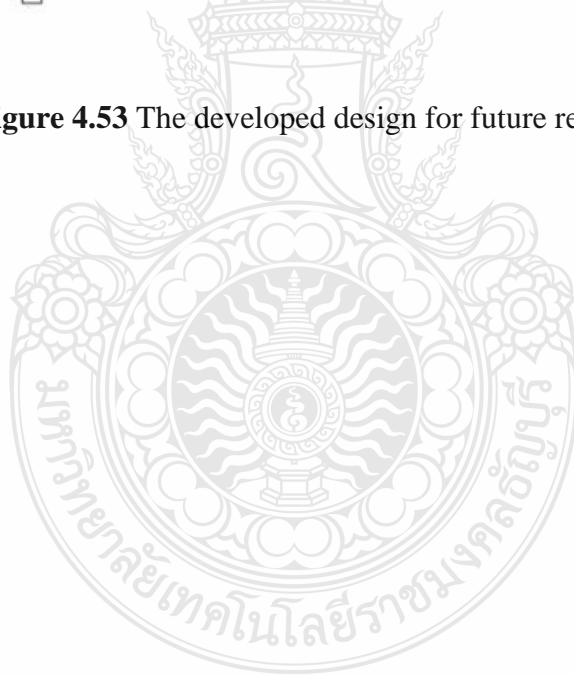
The apparent activation energy and the reaction sequence appear to be converted from 1 to 90%. The clear activation energy increases with more conversions. Reaction to most orders of co-pyrolysis is less than each type of waste lubricant arranged from oil: HDPE> Oil: PS> Oil: PP (less than 1.0 reaction order).

## **5.2 Implication for Practice and Future Research**

To study operation conditions of prototype such as feed flowrate, nitrogen gas flow rate and pressure in the reactor. Because the problem of raw materials rapidly hardens in the feed pump, the prototype should be separated feed raw materials of used lubricant oil and plastic wastes same as this drawing in Fig. 4.53



**Figure 4.53** The developed design for future research



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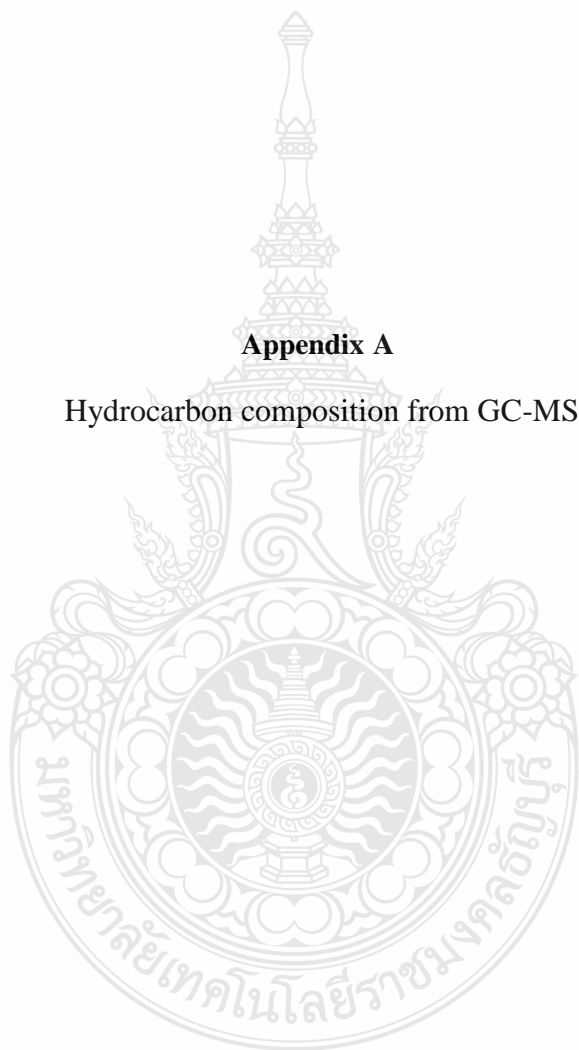




## Appendices

Appendix A: Hydrocarbon composition from GC-MS





**Appendix A**

Hydrocarbon composition from GC-MS

**Table 1A** Hydrocarbon compound of oil product from proportion Oil:PE:PP:PS by GC-MS

| No. | Compound             | % Total     |              |            |            |            |
|-----|----------------------|-------------|--------------|------------|------------|------------|
|     |                      | 50:30:10:10 | 50:30:10:10* | 50:30:20:0 | 50:30:0:20 | 50:0:30:20 |
| 1   | Xylene               |             |              |            |            | 0.737      |
| 2   | 3-methyloctane       |             |              |            |            |            |
| 3   | 2-methyl-1-Octene    |             |              |            |            |            |
| 4   | 1-Nonene             |             |              |            |            |            |
| 5   | Styrene              | 19.136      | 19.338       |            |            | 45.646     |
| 6   | n-Nonane             |             |              |            | 1.658      |            |
| 7   | Nonane               | 1.587       | 1.746        | 1.572      |            |            |
| 8   | Cumene               |             |              |            | 1.077      |            |
| 9   | Benzene              |             |              |            | 34.512     | 1.339      |
| 10  | 2,6-dimethyl-Octane  |             |              | 1.199      |            |            |
| 11  | 4-Methylnonane       |             |              |            |            |            |
| 12  | Methylstyrene        |             |              |            | 6.359      |            |
| 13  | alpha methyl styrene | 4.167       | 3.669        | 2.564      |            | 8.27       |
| 14  | 2-Methyl-1-nonene    |             |              |            |            |            |
| 15  | 1-Decene             | 2.045       | 2.116        | 1.394      | 1.776      |            |

**Table 1A (con't)**

| No. | Compound                       | %wt of Oil:PE:PP:PS |              |            |            |            |
|-----|--------------------------------|---------------------|--------------|------------|------------|------------|
|     |                                | 50:30:10:10         | 50:30:10:10* | 50:30:20:0 | 50:30:0:20 | 50:0:30:20 |
| 16  | n-Decene                       |                     |              |            | 1.344      |            |
| 17  | Decane                         | 1.714               | 1.778        | 1.904      |            |            |
| 18  | Heptane                        |                     |              |            |            | 0.717      |
| 19  | 2,6-dimethylnonane             | 0.423               |              |            |            |            |
| 20  | Octane                         |                     |              |            | 0.898      | 0.982      |
| 21  | 4-Ethylheptane                 |                     |              |            |            |            |
| 22  | 3-methyl-decane                |                     |              |            |            |            |
| 23  | 2-Undecene                     |                     |              | 2.055      |            | 1.211      |
| 24  | 2-methyl-3decene               |                     |              |            |            |            |
| 25  | Cyclopropane                   | 1.756               |              |            |            |            |
| 26  | 1-Undecene                     |                     | 1.733        | 1.805      | 1.274      | 1.382      |
| 27  | 1-heptyl-2-methyl-cyclopropane |                     |              |            |            |            |
| 28  | 3-Heptene                      |                     |              | 2.199      |            |            |
| 29  | Undecane                       | 1.915               | 1.912        | 2.538      | 1.902      | 0.758      |

**Table 1A (con't)**

| No. | Compound            | %wt of Oil:PE:PP:PS |              |            |            |            |
|-----|---------------------|---------------------|--------------|------------|------------|------------|
|     |                     | 50:30:10:10         | 50:30:10:10* | 50:30:20:0 | 50:30:0:20 | 50:0:30:20 |
| 30  | 1,1,3,4-tetramethyl |                     |              |            |            | 0.205      |
| 31  | 1,6-Heptadiene      |                     |              | 2.093      |            |            |
| 32  | 2,6-Ocadienal       |                     | 1.312        |            |            |            |
| 33  | 2-methyl-1-octanol  |                     |              |            |            |            |
| 34  | Z-citral            |                     |              |            |            | 0.676      |
| 35  | 1-Dodecene          |                     | 1.628        | 1.662      |            |            |
| 36  | 2-dodecene          | 1.773               |              |            | 1.409      |            |
| 37  | n-Dodecene          | 2.495               |              |            |            |            |
| 38  | Dodecane            | 0.647               | 2.392        | 3.497      | 1.806      | 0.968      |
| 39  | 1-Tridecene         | 2.429               | 2.572        | 2.033      | 1.472      |            |
| 40  | Tridecane           | 2.548               | 2.262        | 2.462      | 2.047      |            |
| 41  | 2-Decene,7-methyl   |                     | 1.73         |            |            |            |
| 42  | 4-Methyl-2-undecene | 1.396               |              |            |            |            |
| 43  | 1-Octene            |                     |              | 4.087      |            | 2.897      |

**Table 1A (con't)**

| No. | Compound                              | %wt of Oil:PE:PP:PS |              |            |            |            |
|-----|---------------------------------------|---------------------|--------------|------------|------------|------------|
|     |                                       | 50:30:10:10         | 50:30:10:10* | 50:30:20:0 | 50:30:0:20 | 50:0:30:20 |
| 44  | 1,1-dimethyl-2-propyl                 |                     |              |            |            | 1.481      |
| 45  | Caprylene                             |                     |              | 1.995      |            |            |
| 46  | 3-cyclohexanedione                    | 1.517               |              |            |            |            |
| 47  | 4-Isopropyl                           |                     |              |            |            | 3.433      |
| 48  | 3-Ethyl-6-heptafluorobutyryloxyoctane |                     | 1.515        |            |            |            |
| 49  | Tetracontane                          |                     |              |            |            |            |
| 50  | 1-Decanol                             | 1.225               |              |            |            |            |
| 51  | 2-Hexenal                             |                     |              | 1.881      |            |            |
| 52  | Bacchotricuneatin c                   |                     |              |            |            | 1.013      |
| 53  | 3-Cyclohexene                         |                     |              |            |            | 1.295      |
| 54  | 2-Tetradecene                         | 2.214               | 2.35         | 2.652      | 2.116      |            |
| 55  | Tetradecane                           | 2.932               | 3.159        | 3.683      | 2.174      | 1.235      |
| 56  | Pyridinium                            | 1.189               |              |            |            |            |
| 57  | 2-hexyl-1-Decanol                     |                     |              |            |            |            |
| 58  | Cyclotetradecane                      |                     | 1.287        |            |            |            |

**Table 1A (con't)**

| No. | Compound              | %wt of Oil:PE:PP:PS |              |            |            |            |
|-----|-----------------------|---------------------|--------------|------------|------------|------------|
|     |                       | 50:30:10:10         | 50:30:10:10* | 50:30:20:0 | 50:30:0:20 | 50:0:30:20 |
| 59  | n-Undecane            |                     |              | 1.781      |            | 1.781      |
| 60  | 1-Pentadecene         |                     | 2.685        | 2.816      | 1.913      |            |
| 61  | Diocadecyl phosphite  |                     |              |            |            |            |
| 62  | pentadecane           | 2.932               | 3.112        | 3.187      | 2.45       | 0.302      |
| 63  | 1,2,4-trimethyl       |                     |              | 1.080      |            | 1.054      |
| 64  | Tritetracontane       |                     |              |            |            | 0.748      |
| 65  | 6-Tridecene           |                     |              | 2.529      |            |            |
| 66  | Tridecanol            |                     | 1.414        |            |            |            |
| 67  | Borane                | 1.143               |              |            |            | 0.317      |
| 68  | 1-Hexadecene          | 1.686               | 2.099        |            | 1.748      |            |
| 69  | (cis)-2-nonadecene    |                     |              |            |            |            |
| 70  | Cetane                |                     |              |            | 2.403      |            |
| 71  | Hexadecane            | 2.757               | 3.387        | 6.947      |            | 1.835      |
| 72  | 1-chloro-Octadecane   |                     |              |            | 0.895      |            |
| 73  | 1,1-(1,3-propanediyl) |                     |              |            |            | 8.688      |

**Table 1A (con't)**

| No. | Compound                                 | %wt of Oil:PE:PP:PS |              |            |            |            |
|-----|--|---------------------|--------------|------------|------------|------------|
|     |  | 50:30:10:10         | 50:30:10:10* | 50:30:20:0 | 50:30:0:20 | 50:0:30:20 |
| 74  | 1,3-Dephenylpropane                      | 2.412               | 2.857        |            | 4.802      |            |
| 75  | 1-Heptadecene                            |                     |              |            | 2.163      |            |
| 76  | E-14-Hexadecenal                         | 1.357               |              |            |            |            |
| 77  | (cis)-2-nonadecene                       |                     |              |            |            |            |
| 78  | 1,1'-(1-methyl-1,3-propanediyl)          |                     |              |            |            | 2.338      |
| 79  | n-Heptadecene                            |                     |              |            | 2.488      |            |
| 80  | Heptadecane                              | 2.482               | 5.073        | 5.521      |            |            |
| 81  | 3-Benzyl-5-chloro-1,2,3-triazole 1-oxide |                     |              |            | 0.954      |            |
| 82  | 3-Phenyl-1-nitropropane                  |                     |              |            |            | 1.197      |
| 83  | 1-ethyl-2-propyl                         |                     |              |            |            | 1.462      |
| 84  | Cyclopentane                             | 1.428               | 1.396        |            |            | 0.204      |
| 85  | 2-(dodecyloxy)-Ethanol                   |                     |              |            |            |            |
| 86  | 2-Fluoro-2-methylcyclopentanol           |                     |              |            |            | 1.184      |
| 87  | 1-Octanol                                |                     |              | 1.286      |            |            |
| 88  | Tridecanol                               |                     |              |            |            | 0.869      |

**Table 1A (con't)**

| No. | Compound               | %wt of Oil:PE:PP:PS |              |            |            |            |
|-----|------------------------|---------------------|--------------|------------|------------|------------|
|     |                        | 50:30:10:10         | 50:30:10:10* | 50:30:20:0 | 50:30:0:20 | 50:0:30:20 |
| 89  | 1-Octadecene           | 1.199               |              | 2.177      | 1.708      |            |
| 90  | Octadecane             | 2.239               | 4.622        | 3.268      | 2.082      |            |
| 91  | Cyclohexane            |                     |              | 5.27       |            | 1.923      |
| 92  | 2,6-Dodecadiene        |                     |              |            |            | 0.731      |
| 93  | 6-propyl-tridecane     |                     |              |            |            |            |
| 94  | 1-Nonadecene           | 1.053               |              |            |            |            |
| 95  | Tetratriacontane       |                     |              |            |            | 0.312      |
| 96  | nonadecane             | 2.366               | 3.77         | 4.022      | 2.962      | 0.197      |
| 97  | nonahexacontaonic acid |                     |              |            |            |            |
| 98  | 3-Eicasene             | 0.626               |              |            |            |            |
| 99  | Eicosane               | 6.491               | 6.335        | 6.124      | 1.543      | 0.235      |
| 100 | Heneicosane            | 2.595               | 2.141        | 2.907      | 1.81       |            |
| 101 | hexatriacontane        |                     |              |            |            |            |
| 102 | Docosane               |                     | 2.004        | 1.971      | 1.525      | 0.378      |
| 103 | Heptacosane            |                     |              |            |            |            |



**Table 1A (con't)**

| No. | Compound         | %wt of Oil:PE:PP:PS |              |            |            |            |
|-----|------------------|---------------------|--------------|------------|------------|------------|
|     |                  | 50:30:10:10         | 50:30:10:10* | 50:30:20:0 | 50:30:0:20 | 50:0:30:20 |
| 104 | Octacosane       |                     |              |            | 1.365      |            |
| 105 | Dotriacontane    |                     |              | 1.576      |            |            |
| 106 | Tricosane        | 1.302               | 1.612        |            |            |            |
| 107 | 9-Octadecenamide | 6.607               | 4.994        | 3.985      | 3.032      |            |
| 108 | Heptacosane      |                     |              |            |            |            |
| 109 | n-Eicosane       | 5.907               |              | 0.278      | 2.333      |            |
| 110 | Silicic acid     | 0.31                |              |            |            |            |



**Table 2A** Hydrocarbon compound of oil product from proportion Oil:PS by GC-MS

| No | Compound                 | % Total |       |       |       |       |       |        |
|----|--------------------------|---------|-------|-------|-------|-------|-------|--------|
|    |                          | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 1  | Methane                  |         |       |       |       |       | 0.01  |        |
| 2  | 1-Propene,2-methyl       | 0.12    |       | 0.02  | 0.09  | 0.06  |       |        |
| 3  | Acetone                  |         | 0.06  |       | 0.58  |       |       |        |
| 4  | Pentane,2-methyl         |         | 0.02  |       | 0.14  | 0.28  |       |        |
| 5  | Butane,1-chloro-3-methyl |         |       | 0.09  |       |       |       |        |
| 6  | Pentane                  | 0.15    |       |       |       |       |       |        |
| 7  | Pentane,2-methyl         | 0.27    |       | 0.05  |       |       |       |        |
| 8  | 1-Butanol,2,3-dimethyl   | 0.09    |       |       |       |       |       |        |
| 9  | 1-Pentene,2-methyl       | 0.13    |       | 0.07  |       | 0.12  |       |        |
| 10 | Hexane                   | 0.17    | 0.09  | 0.07  | 0.46  | 0.15  |       |        |
| 11 | Cyclopentane, methyl     | 0.03    | 0.02  | 0.03  |       | 0.02  |       |        |
| 12 | Cyclopentane,1-methyl    |         |       |       |       | 0.08  |       |        |
| 13 | 2-Pentene,2,4-dimethyl   | 0.17    |       | 0.05  |       |       |       |        |
| 14 | Pentene,2,4-dimethyl     | 0.13    |       |       |       |       |       |        |
| 15 | Benzene                  |         |       |       |       | 0.14  |       |        |

**Table 2A (con't)**

| No | Compound                               | % Total |       |       |       |       |       |        |
|----|--|---------|-------|-------|-------|-------|-------|--------|
|    |  | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 16 | Butane,2,2,3-trimethyl                 |         | 0.05  |       |       |       |       |        |
| 17 | Pentane,2,4-dimethyl                   |         |       |       |       |       |       |        |
| 18 | Hexane,3-methyl                        | 0.07    | 0.02  | 0.03  | 0.07  | 0.04  |       |        |
| 19 | Cyclopropane,butyl                     | 0.02    |       | 0.12  |       |       |       |        |
| 20 | 1-Heptene                              |         | 0.10  |       |       | 0.14  |       |        |
| 21 | Cycloheptane                           | 0.38    |       |       | 0.28  |       |       |        |
| 22 | Heptene                                | 0.24    |       | 0.09  | 0.24  | 0.13  |       |        |
| 23 | Pentadiene,2,3-dimethyl                | 0.13    | 0.04  | 0.04  |       | 0.05  |       |        |
| 24 | 1-Pentene,2,4,4-trimethyl              | 0.08    | 0.02  |       | 0.07  | 0.02  |       |        |
| 25 | 2-Propenoic acid,2-methyl,methyl ester |         | 0.03  |       | 0.09  |       |       |        |
| 26 | 2-Heptene                              | 0.04    |       |       |       |       |       |        |
| 27 | Cyclohexane, methyl                    | 0.17    | 0.03  | 0.03  | 0.08  | 0.03  |       |        |
| 28 | 2-pentene,2,3,4-trimethyl              | 0.08    | 0.02  | 0.02  | 0.07  |       |       |        |
| 29 | Cyclopentaneethyl                      | 0.18    |       |       |       | 0.03  |       |        |
| 30 | 4-Hepten-1-ol                          |         |       | 0.01  |       |       |       |        |
| 31 | Cyclohexene,4-methyl                   | 0.03    |       |       |       |       |       |        |

**Table 2A (con't)**

| No | Compound                                   | % Total |       |       |       |       |       |        |
|----|--|---------|-------|-------|-------|-------|-------|--------|
|    |  | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 32 | Cyclopentanpropan                          |         |       | 0.01  |       |       |       |        |
| 33 | 1-)1,2-Epoxyethyl (cyclohexane             | 0.04    |       |       |       |       |       |        |
| 34 | Cyclohexane, methylene                     |         | 0.02  |       | 0.05  | 0.02  |       |        |
| 35 | 2-Nonene,3-methyl                          |         |       |       |       | 0.04  |       |        |
| 36 | 1-cis,2-cis,3-trans-trimethyl, cyclopentan | 0.07    |       | 0.02  |       |       |       |        |
| 37 | 1-Hexene,2,5-dimethyl                      | 0.05    |       | 0.02  | 0.10  |       |       |        |
| 38 | 4-Decene,7-methyl                          | 0.12    | 0.05  | 0.04  |       |       |       |        |
| 39 | 1-Octene,3-ethyl                           |         |       |       | 0.10  | 0.07  |       |        |
| 40 | 2-Pentanol,methyl                          | 0.14    |       |       |       |       |       |        |
| 41 | Heptane,2-methyl                           | 0.35    |       |       |       |       |       |        |
| 42 | Benzene,methyl                             |         | 0.86  | 0.94  | 2.81  | 2.74  | 0.26  | 2.60   |
| 43 | Pentane,2,2,4,4-tetramethyl                | 0.12    |       |       |       |       |       |        |
| 44 | Heptane,3-methyl                           | 0.13    | 0.09  | 0.09  |       |       |       |        |
| 45 | Cyclohexane,1,3-dimethyl                   | 2.11    | 2.07  |       |       |       |       |        |
| 46 | 1-Heptene,2-methyl                         | 0.22    | 0.10  | 0.09  | 0.21  | 0.04  |       |        |
| 47 | 1-Octene                                   | 0.27    | 0.18  | 0.11  | 0.32  | 0.16  |       |        |

**Table 2A (con't)**

| No | Compound                              | % Total |       |       |       |       |       |        |
|----|---------------------------------------|---------|-------|-------|-------|-------|-------|--------|
|    |                                       | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 48 | Octane                                | 3.43    | 0.27  | 0.18  | 0.44  | 0.23  |       |        |
| 49 | Cyclopentane,1,2-dimethyl-3-methylene |         | 1.75  | 0.02  |       |       |       |        |
| 50 | Cyclohexene,3,5-dimethyl              |         |       |       |       | 0.06  |       |        |
| 51 | Cyclopropane                          | 0.05    |       |       | 0.05  |       |       |        |
| 52 | 2-Octene                              | 0.05    | 0.03  |       | 0.05  |       |       |        |
| 53 | 4Ethylcyclohexanol                    | 0.03    |       |       |       |       |       |        |
| 54 | Cyclotrisiloxane,hexamethyl           |         | 4.35  | 0.11  | 0.18  | 0.12  |       |        |
| 55 | Cyclohexene,1,2-dimethyl              | 0.11    |       |       |       |       |       |        |
| 56 | 1-Hexacosanol                         | 0.05    | 0.04  | 0.02  | 0.06  |       |       |        |
| 57 | Decane,2-methyl                       |         |       |       |       | 0.02  |       |        |
| 58 | Cyclohexane,1,3,5-trimethyl           |         |       |       |       |       | 0.01  |        |
| 59 | Cyclohexane,ethyl                     | 0.08    | 0.05  | 0.03  | 0.06  | 0.03  |       |        |
| 60 | Cyclohexane,1,1,3-trimethyl           |         |       |       |       | 0.04  |       |        |
| 61 | 2,4-Dimethyl-1-heptene                | 0.14    |       | 0.02  |       |       | 7.14  |        |
| 62 | 1-Octene,3-ethyl                      |         | 0.04  |       |       |       |       |        |
| 63 | Acetic acid,2-ethylhexyl ester        |         |       |       |       | 0.02  |       |        |

**Table 2A (con't)**

| No | Compound                   | % Total |       |       |       |       |       |        |
|----|----------------------------|---------|-------|-------|-------|-------|-------|--------|
|    |                            | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 64 | 1-Heptene,2,6-dimethyl     | 0.24    | 0.15  | 0.11  |       | 0.10  |       |        |
| 65 | 1-Undecene7-methyl         | 0.20    |       |       |       |       |       |        |
| 66 | 4-Undecene,8-methyl        |         |       | 0.08  |       |       |       |        |
| 67 | 5-methyloctene             |         | 0.12  |       |       |       |       |        |
| 68 | 4-Undecene,7-methyl        |         |       |       |       | 0.07  |       |        |
| 69 | Ethylbenzene               |         | 0.90  | 0.74  | 1.84  |       | 0.51  | 1.19   |
| 70 | Bezene,1,4-dimethyl        |         |       |       |       | 2.47  |       |        |
| 71 | Undecane,5-methyl          | 0.29    |       |       |       |       |       |        |
| 72 | Octane,3-methyl            | 0.27    | 0.35  | 0.15  | 0.45  |       |       |        |
| 73 | Heptane,3,5-dimethyl       |         |       |       |       | 0.34  |       |        |
| 74 | 1,2-Cyclohexane dimethanol | 0.07    |       |       |       |       |       |        |
| 75 | Decane,5methyl6methylene   | 0.26    |       |       |       |       |       |        |
| 76 | 1-Nonene                   | 0.27    |       |       |       |       |       |        |
| 77 | Styrene                    |         |       | 3.24  |       |       |       |        |
| 78 | Cis-2-Nonene               | 0.04    |       |       |       |       |       |        |
| 79 | 1,3,5,7-Cyclooctatetraen   |         |       |       |       | 12.27 | 7.80  |        |

**Table 2A (con't)**

| No | Compound                    | % Total |       |       |       |       |       |        |
|----|-----------------------------|---------|-------|-------|-------|-------|-------|--------|
|    |                             | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 80 | Nonane                      | 0.35    |       | 0.37  |       |       |       |        |
| 81 | Phenylacetylene             |         |       |       | 10.36 |       |       |        |
| 82 | Cyclopentane                | 0.09    | 0.17  |       |       |       |       |        |
| 83 | 1-Undecanol                 | 0.08    |       |       |       |       |       |        |
| 84 | 5-Dodecene                  |         |       | 0.09  |       |       |       |        |
| 85 | 2-Nonene                    |         | 0.24  |       |       |       |       |        |
| 86 | 1-Propene,2-methyltetramer  |         |       | 0.14  |       |       |       |        |
| 87 | Pentane,2,2,3,3-tetramethyl | 0.07    |       |       |       |       |       |        |
| 88 | Benzene,)1-methylethyl(     |         | 0.32  | 0.26  | 0.64  | 0.82  | 0.13  | 33.02  |
| 89 | Dodecane,2-cyclohexyl       | 0.08    |       |       |       |       |       |        |
| 90 | Dodecane,4-cyclohexyl       |         |       | 0.08  |       |       |       |        |
| 91 | Cyclohexane, propyl         |         | 0.12  |       |       |       |       |        |
| 92 | Nonane,3-methyl             | 0.10    | 0.14  | 0.08  | 0.13  |       |       |        |
| 93 | 2-Ethylhexyl                |         |       |       |       | 0.07  |       |        |
| 94 | 4-Undecene,8-methyl         |         |       |       | 0.17  |       |       |        |
| 95 | Octane,4,5-dipropyl         |         |       |       |       | 0.07  |       |        |

**Table 2A (con't)**

| No  | Compound                    | % Total |       |       |       |       |       |        |
|-----|-----------------------------|---------|-------|-------|-------|-------|-------|--------|
|     |                             | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 96  | Octane,3-methyl-6-methylene | 0.20    |       |       |       |       |       |        |
| 97  | Benzene,2-propenyl          |         |       | 0.21  |       | 0.26  | 0.10  |        |
| 98  | Benzene,1propenyl           |         | 0.31  |       | 0.33  |       |       | 0.19   |
| 99  | 3-Undecene, 6-methyl        | 0.15    |       |       |       |       |       |        |
| 100 | Benzene,propyl              |         |       | 0.28  | 0.38  | 0.28  | 0.05  | 0.04   |
| 101 | 1-Octene,2,6-dimethyl       | 1.03    | 0.38  |       |       |       |       |        |
| 102 | 1-Hexene,3,5,5-trimethyl    | 0.23    |       | 0.31  |       |       |       |        |
| 103 | Octane,2,5-dimethyl         |         |       |       | 0.38  |       |       |        |
| 104 | Benzaldehyde                |         |       |       |       |       | 1.16  |        |
| 105 | Hexadecane                  | 0.14    |       |       |       |       |       |        |
| 106 | Octane 3,6-dimethyl         | 0.19    | 0.27  | 0.16  |       | 0.12  |       |        |
| 107 | 2-Methyl-nonene             | 0.05    |       |       |       |       |       |        |
| 108 | 3-Undecene,4-methyl         |         | 0.18  |       |       |       |       |        |
| 109 | Pentane, 3,3-diethyl        | 0.06    |       |       |       |       |       |        |
| 110 | 1-Undecene,2-methyl         | 0.27    |       |       |       |       |       |        |
|     |                             |         |       |       |       |       |       |        |



**Table 2A (con't)**

| No  | Compound                         | % Total |       |       |       |       |       |        |
|-----|----------------------------------|---------|-------|-------|-------|-------|-------|--------|
|     |                                  | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 111 | Benzene                          |         | 1.85  | 1.95  | 3.84  | 3.58  | 3.38  | 4.19   |
| 112 | Cyclopropane                     | 0.28    | 0.40  |       |       |       |       |        |
| 113 | Cyclopropanenonyl                |         |       | 0.43  |       |       |       |        |
| 114 | 1-propenyl                       |         | 0.37  | 0.34  | 0.40  | 0.38  | 0.72  | 0.02   |
| 115 | Benzene,1,3,5-trimethyl          | 0.10    | 0.23  |       |       |       |       |        |
| 116 | Decane                           |         |       |       |       |       | 2.01  |        |
| 117 | Tetradecane                      |         |       |       |       | 0.30  |       |        |
| 118 | Tridecane                        | 0.37    | 0.64  | 0.37  | 0.50  |       |       |        |
| 119 | 5-Dodecene                       | 0.16    |       |       |       |       |       |        |
| 120 | 5-Dodecane                       |         |       |       |       | 0.11  |       |        |
| 121 | Cyclooctane                      |         | 0.25  |       | 0.19  |       |       |        |
| 122 | Propanoic acid, 2-propenyl ester |         |       |       |       |       | 0.02  |        |
| 123 | 1-Decene 3,4-dimethyl            | 0.20    | 0.36  | 0.24  |       | 0.19  |       |        |
| 124 | Octane 1,1-oxybis                |         |       |       | 0.28  |       |       |        |
| 125 | Heptane 3,3,5-trimethyl          | 0.17    | 0.29  |       | 0.19  |       |       |        |
| 126 | Heptane 2,5,5-trimethyl          |         |       | 0.18  |       |       |       |        |

**Table 2A (con't)**

| No  | Compound                          | % Total |       |       |       |       |       |        |
|-----|-----------------------------------|---------|-------|-------|-------|-------|-------|--------|
|     |                                   | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 127 | 4-Octen-3-one                     |         |       | 0.25  |       |       |       |        |
| 128 | Cyclohexane,1-bromo-3-methyl      | 0.26    | 0.39  |       | 0.26  |       |       |        |
| 129 | Nonane,3,7-dimethyl               |         | 0.10  | 0.08  | 0.07  | 0.06  |       |        |
| 130 | 3-Undecene, 4-methyl              | 0.14    |       |       |       |       |       |        |
| 131 | Benzene,3-butenyl                 |         |       |       |       | 0.16  | 0.19  | 0.17   |
| 132 | 2-Decene 4-methyl                 |         |       | 0.18  |       |       |       |        |
| 133 | 3-Undecene 4-methyl               |         | 0.26  |       |       |       |       |        |
| 134 | Heptane 1-chloro                  |         |       |       | 0.20  |       |       |        |
| 135 | Cyclopentane 3-hexyl 1,1-dimethyl | 0.29    | 0.45  | 0.32  | 0.28  |       |       |        |
| 136 | Octane 2,3,6,7-tetramethyl        |         |       |       |       | 0.11  |       |        |
| 137 | 6-Methylundecane                  | 0.27    |       |       |       |       |       |        |
| 138 | Benzene,2,3-dimethyldecyl(        |         |       | 0.53  | 0.50  |       |       |        |
| 139 | Benzene, butyl                    |         |       |       |       | 0.31  |       |        |
| 140 | Heptane,2,2,3,3,5,6,6-heptamethyl |         | 0.68  |       |       |       |       |        |
| 141 | Benzene,1-methylenepropyl(        |         |       |       |       |       | 0.13  | 0.10   |
| 142 | Heptane,2,5,5-trimethyl           | 0.12    |       |       |       |       |       |        |

**Table 2A** (con't)

| No  | Compound                       | % Total |       |       |       |       |       |        |
|-----|--------------------------------|---------|-------|-------|-------|-------|-------|--------|
|     |                                | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 143 | Acetophenone                   |         |       |       |       |       | 1.00  |        |
| 144 | Nonane,5-)1-methylpropyl(      |         |       | 0.20  |       | 0.11  |       |        |
| 145 | Decane,3-methyl                | 0.14    |       |       |       |       |       |        |
| 146 | Nonane,5-)2-methylpropyl(      |         | 0.31  |       |       |       |       |        |
| 147 | Undecane,3,4-dimethyl          |         |       |       | 0.28  |       |       |        |
| 148 | Cyclopropane,1-)1-methylethyl( | 0.03    |       |       |       |       |       |        |
| 149 | Tetrapropylene                 |         |       |       |       | 0.09  |       |        |
| 150 | Octadecane,chloro              |         |       | 0.13  |       |       |       |        |
| 151 | 1-Nonanol,4,8-dimethyl         |         |       |       |       |       | 0.01  |        |
| 152 | Tridecanol                     |         | 0.24  |       |       |       |       |        |
| 153 | 1-Dodecane 1,3,7,11-trimethyl  |         |       |       | 0.14  |       |       |        |
| 154 | 2-Undecene,4,5-dimethyl        | 0.09    |       |       |       |       |       |        |
| 155 | Tridecane,7-methylene          |         |       |       |       | 0.16  |       |        |
| 156 | Decane,5-methyl 6-methylene    |         | 0.52  | 0.35  | 0.33  |       |       |        |
| 157 | 1Undecene,2methyl              | 0.30    |       |       |       |       |       |        |
| 158 | Cyclopropanenonyl              |         |       |       |       | 0.20  |       |        |

**Table 2A (con't)**

| No  | Compound                          | % Total |       |       |       |       |       |        |
|-----|-----------------------------------|---------|-------|-------|-------|-------|-------|--------|
|     |                                   | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 159 | 1-Iodo-2-methylundecane           |         |       |       |       |       |       | 2.03   |
| 160 | Benzene,(3,3-dimethyl-4-pentenyl) |         |       |       |       | 0.10  |       |        |
| 161 | 4-Undecanol,7-ethyl-2-methyl      |         |       | 0.20  | 0.24  |       |       |        |
| 162 | 1-Hexanol,2ethyl                  | 0.14    |       |       |       |       |       |        |
| 163 | Benzene,(1-Formylethyl)           |         |       |       |       |       | 0.08  |        |
| 164 | 5-Undecene, 9-methyl              |         | 0.29  |       |       |       |       |        |
| 165 | 1-Undecene, 5-methyl              |         | 0.22  | 0.14  | 0.08  |       |       |        |
| 166 | 5-Undecene                        |         | 0.21  |       | 0.12  |       |       |        |
| 167 | Octane,2,6dimethyl                |         |       | 0.35  |       |       |       |        |
| 168 | Benzene,)2-methyl(                |         |       |       |       | 0.11  | 0.14  |        |
| 169 | Undecene,5-methyl                 |         | 0.33  |       |       |       |       |        |
| 170 | Benzene,)1-methyl-propanyl(       |         |       |       | 0.21  |       |       |        |
| 171 | Benzene,)2-decyldodecyl(          |         |       |       |       | 0.15  |       |        |
| 172 | Nonane,5-)2-methylpropyl(         | 0.44    | 0.48  | 0.25  |       |       |       |        |
| 173 | Benzene,)3-methylbuyl(            |         | 0.23  | 0.17  | 0.15  | 0.10  |       |        |
| 174 | Nonane,5-butyl                    | 0.16    |       |       |       |       |       |        |

**Table 2A (con't)**

| No  | Compound                          | % Total |       |       |       |       |       |        |
|-----|-----------------------------------|---------|-------|-------|-------|-------|-------|--------|
|     |                                   | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 175 | Nonane,5-methyl-5-propyl          |         | 0.33  |       |       |       |       |        |
| 176 | Undecane,3-methyl                 |         | 0.14  | 0.19  | 0.17  |       |       |        |
| 177 | Cyclopentane,3-hexyl-1,1-dimethyl | 0.26    |       |       |       | 0.12  |       |        |
| 178 | Tridecane,7-methylene             |         | 0.52  | 0.28  |       |       |       |        |
| 179 | Benzene,)3-methyl-3-butenyl(      |         |       |       | 0.27  |       |       |        |
| 180 | 1-Octanol,dimethyl                |         |       | 0.58  |       |       |       |        |
| 181 | 7-Tetradecene                     | 0.41    |       |       |       |       |       |        |
| 182 | Undecene,9methyl                  |         | 0.77  |       |       |       |       |        |
| 183 | Benzene,)1-methylenbutyl(         |         |       |       |       |       | 0.06  | 3.74   |
| 184 | Benzene,4-pentenyl                |         |       |       |       |       | 0.09  |        |
| 185 | Octadecane, 1-chloro              |         |       |       |       | 0.20  |       |        |
| 186 | 1-Octanol,2butyl                  | 0.26    | 0.52  | 0.36  | 0.40  |       |       |        |
| 187 | Penylbenzene,                     |         |       |       | 0.46  | 0.22  |       |        |
| 188 | Benzene,undecyl                   |         |       | 0.26  |       |       |       |        |
| 189 | Benzene,)2,2-dimethylbutyl(       |         | 0.39  |       |       |       |       |        |
| 190 | 10-Chloro-1-decanol               |         |       | 0.07  |       |       |       |        |

**Table 2A (con't)**

| No  | Compound                          | % Total |       |       |       |       |       |        |
|-----|-----------------------------------|---------|-------|-------|-------|-------|-------|--------|
|     |                                   | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 191 | Undecane,4,5-dimethyl             |         |       | 0.15  |       |       |       |        |
| 192 | Zingberene                        | 0.12    |       |       |       |       |       |        |
| 193 | Benzoic acid                      |         |       |       |       |       | 0.14  |        |
| 194 | 1-Undecene,2-methyl               | 0.58    | 1.38  | 0.97  | 0.84  | 0.16  |       |        |
| 195 | Azulene                           |         |       |       |       |       | 0.12  |        |
| 196 | Cyclobutane,3hexyl1,1,2-trimethyl |         |       |       |       |       |       | 0.02   |
| 197 | 1-Dodecene                        |         |       |       |       | 0.28  |       |        |
| 198 | 1-Dodecanol                       | 0.68    | 0.90  | 0.62  | 0.71  |       |       |        |
| 199 | Dodecane                          | 0.46    | 1.06  | 0.68  | 0.46  | 0.37  |       |        |
| 200 | 5-Undecene,9-methyl               |         | 0.38  | 0.25  |       |       |       |        |
| 201 | 5Undecene,3methyl                 |         | 0.48  |       | 0.21  |       |       |        |
| 202 | Undecene,2,5-dimethyl             | 0.45    | 0.71  | 1.11  | 0.31  | 0.22  |       |        |
| 203 | Decanedioic acid,dideclester      |         |       |       |       | 0.12  |       |        |
| 204 | 1H-Indene,1-ethyl-2,3-dihydro     |         |       |       |       | 0.10  |       |        |
| 205 | 1-Octanol,2butyl                  | 0.09    |       |       |       |       |       |        |

**Table 2A** (con't)

| No  | Compound                                | % Total |       |       |       |       |       |        |
|-----|---|---------|-------|-------|-------|-------|-------|--------|
|     |   | 100:0   | 75:25 | 60:40 | 50:50 | 40:60 | 0:100 | 0:100* |
| 206 | Benzene,)3,3-dimethyl-1-methylenebutyl( |         |       |       |       |       |       | 0.03   |
| 207 | Carbonic acid butyl ester octyl ester   |         |       | 0.49  | 0.35  |       |       |        |
| 208 | 2-Undecene,6-methyl                     | 0.14    | 0.52  | 0.41  |       |       |       |        |
| 209 | 1-Hexene,2-phenyl                       |         |       |       | 0.30  | 0.17  |       |        |
| 210 | Cyclooctane,1,5-dimethyl                |         | 0.57  |       |       |       |       |        |
| 211 | 3-Haxadecene                            | 0.22    |       |       |       | 0.09  |       |        |
| 212 | 1-Undecene, 9-methyl                    | 0.39    |       | 0.26  |       |       |       |        |
| 213 | 1-Propanone, 1-phenyl                   |         |       |       |       |       | 0.06  |        |
| 214 | 1-Octanol,2,7-dimethyl                  | 4.02    |       |       | 0.19  |       |       |        |
| 215 | 1-Octanol,3,7-dimethyl                  |         | 0.32  |       |       |       |       |        |
| 216 | Dodecane,6-methyl                       |         | 0.77  |       |       |       |       |        |
| 217 | Benzene,)3,3-dimethyl-4-pentenyl(       |         |       |       |       | 0.09  |       |        |
| 218 | Undecane, 3,4-dimethyl                  | 0.21    |       |       |       |       |       |        |
| 219 | Dodecane 4-methyl                       | 1.74    | 0.31  | 0.23  | 0.16  |       |       |        |
| 220 | Benzene,hexyl                           |         |       |       |       | 0.22  |       |        |

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