THERMAL AND CATALYTIC PYROLYSIS OF MUNICIPAL PLASTICS WASTE FROM SAMUI ISLAND LANDFILL

Jiraphan Chotiratanasak[1, 2], Tharapong Vitidsant[3] and Maneerat Khemkhao[1, *]

[1] Rattanakosin College for Sustainable Energy and Environment,
Rajamangala University of Technology Rattanakosin
[2] E-Square Green Innovation Co., Ltd.
[3] Department of Chemical Technology, Faculty of Science, Chulalongkorn University

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Abstract

Plastic waste is the largest component of municipal solid waste (MSW) on Samui Island, which still has many management problems. Pyrolysis is an interesting technology that could help reduce plastic waste by converting it into more valuable fuels. Therefore, the focus of this research was to convert plastic waste from Samui Island into fuel via the thermal pyrolysis and catalytic pyrolysis processes. The pyrolysis reaction was carried out at various temperatures (390, 425, 450, and 475 °C) with and without a catalyst in a 3-L bench-scale reactor to determine the optimal condition that produced the highest yield of pyrolysis oil. The raw material was a 1:1 weight ratio of high-density polyethylene (HDPE) and polypropylene (PP) plastic wastes, and the catalyst was 3 wt.% spent fluid catalytic cracking (FCC). The reaction time was determined until there was no liquid product left. The results revealed that 450 °C was the optimal temperature for both the thermal pyrolysis and catalytic pyrolysis, with the highest pyrolysis oil yields of 84.21% and 70.12%, respectively.

* Corresponding Author: Maneerat Khemkhao
Email: maneerat.khe@rmutr.ac.th

The pyrolysis oil components for the thermal pyrolysis were 37.00% naphtha, 18.60% kerosene, 37.40% diesel, and 7.00% long residue, while the catalytic pyrolysis were 39.90% naphtha, 17.10% kerosene, 35.40% diesel, and 7.60% long residue. Furthermore, thermal pyrolysis took longer than catalytic pyrolysis to complete.

Keywords: Thermal Pyrolysis and Catalytic Pyrolysis, Plastic Waste, Spent FCC Catalyst, Samui Island

Introduction

Samui Island has been recognized as one of Thailand's most popular tourist destinations. Many visitors have come and stayed, contributing to an increase in the volume of MSW. According to the feasibility study of the model and approach for municipal solid waste disposal in Samui Island City Municipality, MSW produced on the island is approximately 150 tons per day, and MSW dumped in landfills is approximately 300,000 tons, with plastic waste accounting for 40.4% and 64.4% of the daily and dumped MSW, respectively (TISTR, 2020). Nowadays, MSW has been compressed and wrapped with low-density polyethylene (LDPE) plastic before being shipped via ferries to a landfill in Surat Thani province. However, due to a limited area, leachate contamination of the environment, and being relatively expensive, Furthermore, there are risks of accidents during transportation. For example, in August 2020, a ferry capsized, causing 60 tons of Samui Island MSW to sink into the sea during transportation from Samui Island to Surat Thani province (Thai PBS, 2020). As a result, an appropriate MSW management strategy, particularly for plastic waste, is required.

Pyrolysis is a potential alternative technology for disposing of plastic waste by thermally degrading long-chain hydrocarbons into shorter-chain

hydrocarbons in the absence of oxygen at temperatures ranging from 300 to 600 ºC (Lee et al., 2021; Singh et al., 2019; Zhang et al., 2020). This method converts plastic waste into more valuable fuels such as pyrolysis oil, pyrolysis gas, and residue carbon (Hakeem et al., 2018; Maafa, 2021).

Several factors influence plastic pyrolysis yield and selectivity, such as temperature, retention time, type of raw materials, catalyst-to-feed ratio, and type of catalysts. Various studies have been done on thermal pyrolysis and catalytic pyrolysis using different raw materials and catalysts to look at the yield and selectivity of products. Zn, ZnO, and $ZnCl_2$ were used as catalysts in the catalytic pyrolysis of expanded polystyrene waste (EPSW); Zn produced more pyrolysis oil yield and product selectivity, such as toluene, ethylbenzene, and styrene, than any other catalyst and more than thermal pyrolysis (Adnan et al., 2014). Furthermore, using catalysts reduced the reaction temperature and time compared to thermal pyrolysis. In a while, Hakeem et al. (2018) used Ahoko kaolin as a catalyst in the thermal pyrolysis and catalytic pyrolysis of PP plastic waste. They found out that the Ahoko kaolin catalyst worked well to convert PP plastic waste into pyrolysis oil, which provided a higher pyrolysis oil yield than the thermal pyrolysis. In the work of Panda (2018), he used calcium bentonite as a catalyst in the thermal pyrolysis and catalyst pyrolysis of PP, LDPE, HDPE, and mixed PP, LDPE, and HDPE in a 1:1:1 ratio to investigate the effect of temperature and catalyst concentration on product yield. He discovered that the highest yield of pyrolysis oil from all plastics was obtained at 500 ℃ for both thermal and catalytic pyrolysis. In addition, increasing the catalyst concentration resulted in a shorter reaction time. However, overuse of catalysts resulted in a lower pyrolysis oil yield and a higher gas yield. Miandad et al. (2017a) conducted the thermal pyrolysis of PE, PP, PS, and polyethylene terephthalate (PET) plastic wastes to study the effect of different plastic waste types on the yield of pyrolysis oil. At 450 ℃ and 75 minutes of retention time,

all types of plastic waste were converted into liquid oil, except for PE, which was converted into wax because it has long carbon chains. However, the pyrolysis of mixed plastic PS, PP, PE in a ratio of 50/25/25% provided a lower wax content due to free radicals produced from PS degradation that promoted cracking in PE plastic. In addition, using a catalyst helps reduce wax formation in the pyrolysis oil of PE (Miandad et al., 2017b).

In petroleum refineries, FCC catalyst, which is Y-zeolite, converts heavy petroleum fractions into lighter products such as gasoline, diesel, and other products. Approximately 150,000–170,000 tons of spent FCC catalyst are generated annually as waste and are typically disposed of in landfills (Chiranjeevi et al., 2016). Some researchers have employed a fresh FCC catalyst in catalytic pyrolysis, such as Kassargy et al. (2018), who used USY zeolite in the catalytic pyrolysis of PE, PP, and mixed PE and PP plastic waste, which increased the gas product. Meanwhile, Singh et al. (2020) used a zeolite catalyst in the catalytic pyrolysis of LDPE plastic waste, which produced superior quality pyrolysis oil compared to oil obtained from thermal pyrolysis.

According to the large amount of spent FCC discarded as previously mentioned, the reuse of spent FCC catalyst is still expected to lower the costs of procuring new catalysts, reduce efforts in developing proprietary or new catalysts, and improve the overall process economy. A spent FCC catalyst has been used in some research on thermal and catalytic pyrolysis. Aisien et al. (2021) employed a spent FCC catalyst in the catalytic pyrolysis of PP plastic waste and compared it to thermal pyrolysis. They found that thermal pyrolysis provided the highest yield of pyrolysis oil. While in the catalytic process, the pyrolysis oil yield decreased and the gas yield increased with the increasing amount of catalyst, which was contributed by the highly acidic behavior that led to further cracking of liquid hydrocarbons. Saeaung et al. (2021) used spent FCC in the thermal and catalytic pyrolysis of petroleum-based plastics (HDPE,

LDPE, PP) and biodegradable polymers, polylactide (PLA). They found that the pyrolysis oil from the thermal pyrolysis of HDPE and LDPE provided a high yield of waxes, whereas the pyrolysis oil from PP and PLA provided both waxes and liquid oil. The results also exhibited that spent FCC catalyst reduced the production of waxes and increased the production of gasoline-range hydrocarbons and aromatics.

Regarding the related literature mentioned above, the yield and selectivity of plastic pyrolysis products from thermal pyrolysis and catalytic pyrolysis still varied depending on process factors. However, plastic waste from landfills is complex, and there are differences in composition from any landfill that might affect the pyrolysis reaction and product selectivity. Therefore, this research aimed to study the effects of reaction temperature on yield and components of pyrolysis products from thermal and catalytic pyrolysis of mixed plastic wastes, HDPE and PP, by using spent FCC catalyst in the catalytic process.

Materials and Methods

The raw material was a 1:1 weight ratio of HDPE and PP plastic waste from Samui Island collected from the sorting machine. The plastic waste was crushed into smaller pieces (around 3 cm) and dried with hot air to reduce moisture and bulk volume. In the catalytic process, the spent FCC was used as a catalyst. The pyrolysis reaction was carried out in a 3-L bench-scale reactor at temperatures of 390, 425, 450, and 475 °C, as shown in Fig. 1. Fig. 2 shows the pyrolysis process flow diagram, which includes the feeding entrance, reactor, and condenser. 250 g of the raw material was fed into the reactor. In the catalytic process, 3 wt.% of spent FCC catalyst was fed into the reactor along with the raw materials. After feeding, the plastic waste was heated and degraded into a vapor product. The vapor flowed through the condenser and condensed into a liquid oil product, which was collected in the storage container.

Non-condensable vapor flowed into the flare. Finally, carbon residues that were left in the reactor were collected and weighted after cooling down the reactor. The reaction time was determined when there was no product output. The pyrolysis oil and residue carbon were collected and weighed, while the pyrolysis gas was calculated from the mass balance.

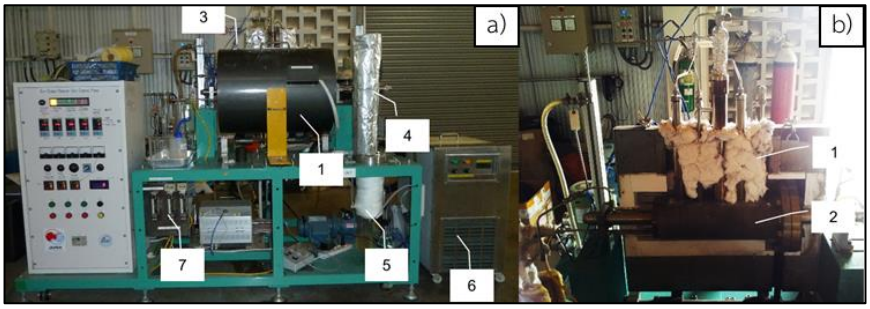


Fig. 1 The bench-scale reactor, a) overall equipment, and b) focusing on the reactor and heater, including: 1. Electric heater with a controller, 2. Horizontal reactor with agitator, 3. K-type thermocouple, 4. Condenser, 5. Liquid product storage, 6. Chiller, and 7. N_2 flow controller.

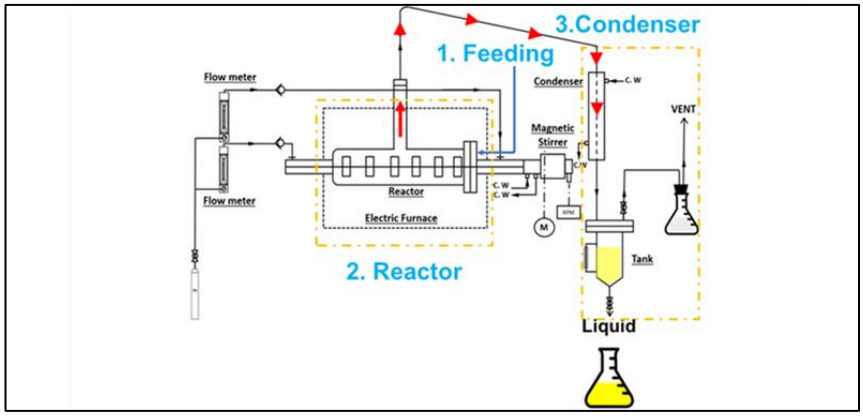


Fig. 2 The pyrolysis process flow diagram.

After that, pyrolysis oil was analyzed by Distillation Gas Chromatography (DGC) to determine the fractions of naphtha, kerosene, diesel, and long residue. Furthermore, the HDPE and PP plastic wastes were analyzed for the thermal degradation temperature of individual plastics by thermogravimetric analysis (TGA). The BET surface area, pore volume, and pore size of the spent FCC were analyzed by the surface area and porosity analyzer. The catalyst type and composition of spent FCC catalyst were also analyzed by X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) methods, respectively.

Results and Discussion

The TGA results for HDPE and PP plastic wastes are shown in Fig. 3. Their degradation temperatures ranged between 400 and 500 °C. The peak degradation temperatures of HDPE and PP plastic waste were 480.2 °C and 467.7 °C, respectively. Focusing on the peak degradation temperatures, it was observed that the temperature of PP was lower than HDPE. Because the polymer structure of PP contained more pendant methyl groups than the structure of HDPE. It is the reason why the PP structure is more easily degraded than the HDPE structure, which has a linear chain structure and a dense structure (Lee et al., 2021; Maafa, 2021).

The BET surface area, the pore volume, and the pore size of the spent FCC catalyst were 101.03 m^2/g, 0.09 cm^3/g, and 37.13 Å, respectively. In the X-ray Diffraction (XRD) analysis depicted in Fig. 4, it was demonstrated that the diffraction peak of the spent FCC catalyst (the solid line in Fig. 4) was similar to the diffraction peak of the Ultra Stable Y Zeolite (USY) pattern, which is a standard y-type zeolite from the database (Baerlocher & McCusker, 2016). Therefore, it was assumed that the spent FCC catalyst is a y-type zeolite that is used in petroleum refineries to convert heavy petroleum fractions into lighter products. In addition, X-ray fluorescence (XRF) revealed that the molar ratio

of SiO_2 to Al_2O_3 was 1, and there were some other metals such as La (3.19%) and Mg (1.44%), which likely were components in heavy oil.

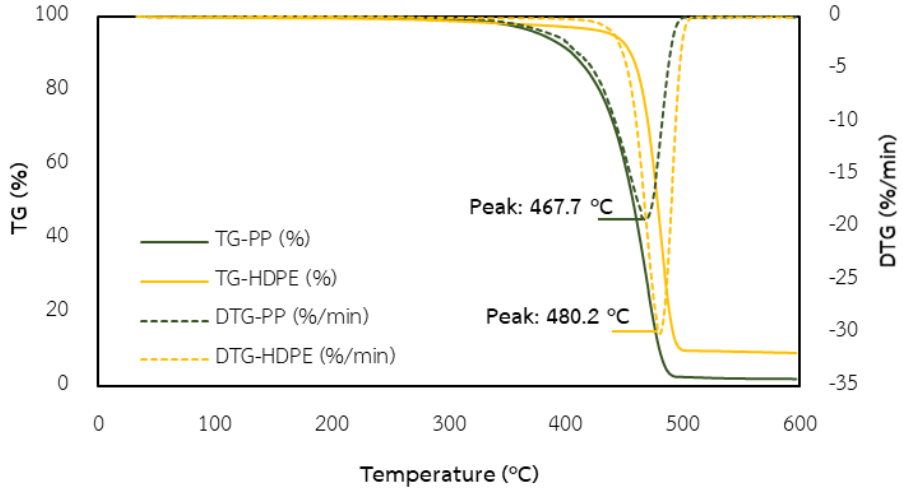


Fig. 3 The TGA results of HDPE and PP plastic wastes.

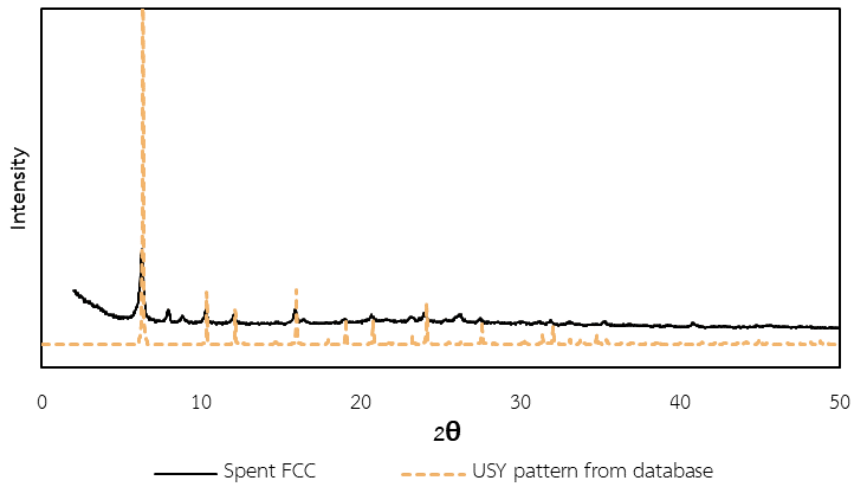


Fig. 4 The XRD results of the spent FCC catalyst and USY pattern form data base (Baerlocher & McCusker, 2016).

The liquid product profiles of thermal pyrolysis and catalytic pyrolysis are shown in Figs. 5 and 6, respectively. Both figures showed the weight of the collected product every 15 minutes in the dashed line and the accumulated weight of the liquid product in the solid line. In the case of the dashed line, the tall and thin peak showed that the pyrolysis occurred in a short time. On the other hand, the peak that appeared in the small and wide base could indicate slow pyrolysis due to low supply energy. In addition, the accumulation line (solid line), especially the end of that line, referred to the time at the finish of the pyrolysis process. Moreover, the profiles of both figures demonstrated that increases in reaction temperature affected creaking behavior in the pyrolysis process.

The amount of pyrolysis oil produced by thermal pyrolysis increased as the reaction temperature rose (Fig. 5). However, at 390 °C of reaction temperature, both the thermal and catalytic pyrolysis did not seem to show any liquid product, as shown in Figs. 5 and 6, due to the lower reaction temperature than the degradation temperature analyzed by TGA in Fig. 3.

Fig. 6 shows the results of the liquid product of catalytic pyrolysis. The liquid product profiles were revealed with the same trend of thermal pyrolysis as in Fig. 5. Moreover, it might be evident that the plastic sample cracked rapidly when the temperature increased in both processes due to the endothermic reaction of the pyrolysis process.

However, as shown in Fig. 7, the catalytic process had a shorter reaction time than the thermal process. The time required to terminate the reaction in the thermal process was more than the catalytic process, which principally accelerates the reaction of the catalyst.

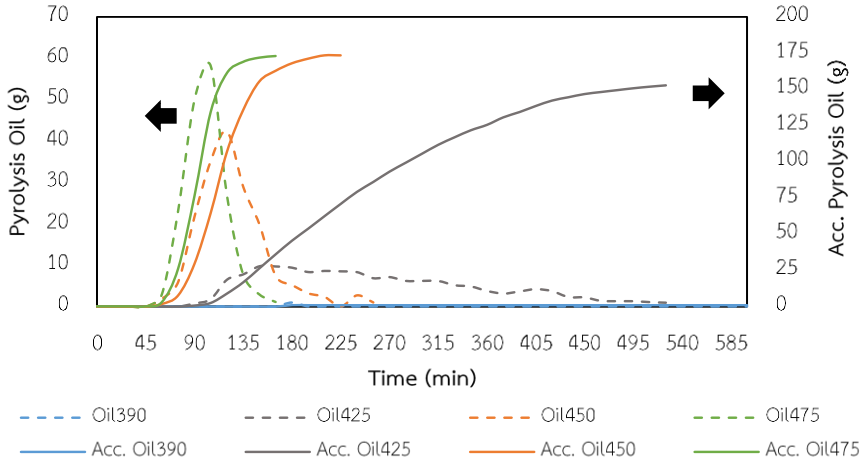


Fig. 5 The liquid product profile and reaction time of thermal pyrolysis.

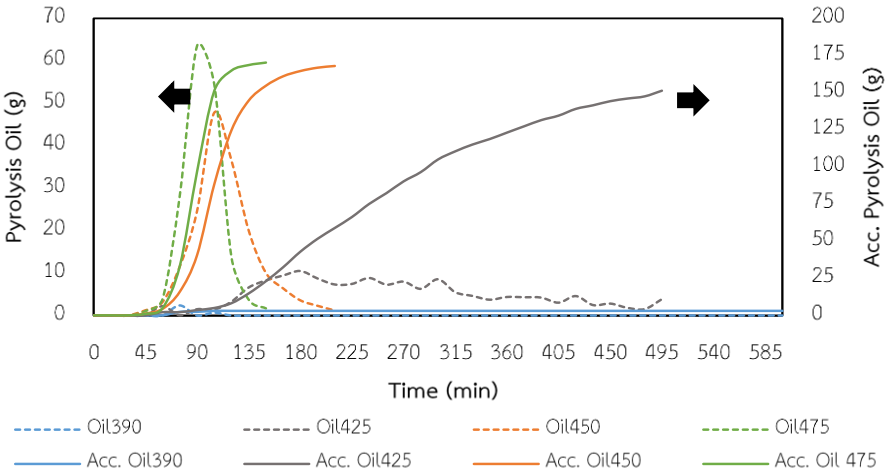


Fig. 6 The liquid product profile and reaction time of catalytic pyrolysis.

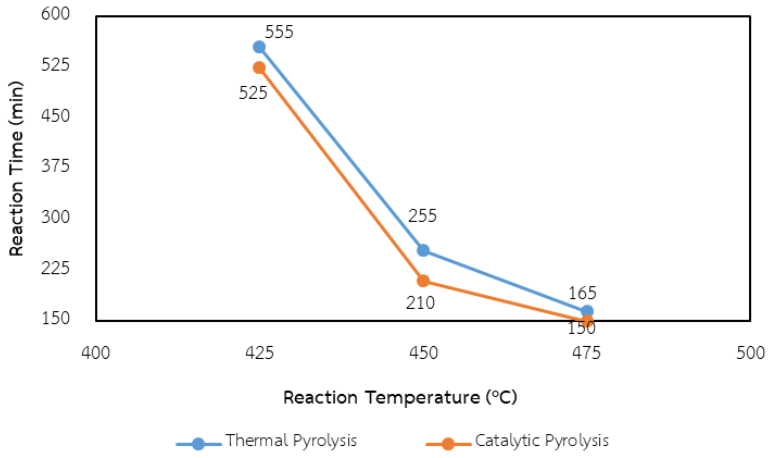


Fig. 7 The reaction time and reaction temperature in the thermal pyrolysis and catalytic pyrolysis.

Table 1 summarizes the pyrolysis experiment results. In the case of pyrolysis oil yield, the result showed that the increase in reaction temperature in the catalytic process resulted in an increase in liquid yield from 63.63 to 70.12 wt.% and a likely constant value of 475 °C. In contrast, the product of the thermal process had a maximum liquid yield (84.21 wt.%) at 450 °C. The higher liquid yield from thermal pyrolysis than catalytic pyrolysis is probably due to the high activities of the spent FCC catalyst, which promoted the pyrolysis reaction; thus, the liquid product could be cracked into more gas, which increased from 3.98 to 21.56 wt.% in thermal pyrolysis and catalytic pyrolysis at 450 °C, respectively. The liquid product of all experiments was analyzed by the composition of DGC, and their results are also shown in Table 1. The composition of liquid products can be separated by the range of their boiling points, which were defined as naphtha (25–200 °C), kerosene (200–250 °C), diesel (250–370 °C), and long residue (>370 °C).

Therefore, the optimum condition for the catalytic process was at 450 °C which provided 70.12 wt.% of liquid yield, 39.90% of naphtha, 17.10% of

kerosene, 35.40% of diesel, and 7.60% of long residue. In comparison, the optimum temperature for the thermal process was 450 ºC, which contributed 84.21% of the yield, 37.00% of the naphtha, 18.60% of the kerosene, 37.40% of the diesel, and 7.00% of the long residue. However, due to the low decomposition temperature of the plastic, the liquid product was not found at 390 ºC in either process. Furthermore, the time required to terminate the reaction in the thermal process was longer than in the catalytic- process because the catalyst can accelerate the reaction.

Table 1 Product yields, pyrolysis oil compositions, and reaction time.

Reaction Conditions	Thermal Pyrolysis				Catalytic Pyrolysis			
Reaction temperature (°C)	**390**	**425**	**450**	**475**	**390**	**425**	**450**	**475**
Product yields (wt.%)								
Pyrolysis oil	0	42.35	84.21	73.38	0	63.63	70.12	70.05
Residue carbon	0	17.25	11.81	8.90	0	14.81	12.04	9.63
Pyrolysis gas*	0	40.40	3.98	17.72	0	21.56	17.84	20.32
Total	-	100	100	100	-	100	100	100
Pyrolysis oil compositions (vol.%)								
Naphtha	0	37.80	37.00	33.40	0	47.00	39.90	34.80
Kerosene	0	22.40	18.60	15.50	0	23.30	17.10	14.90
Diesel	0	38.70	37.40	35.30	0	28.80	35.40	34.00
Long residue	0	1.10	7.00	15.80	0	0.90	7.60	16.30
Total	-	100	100	100	-	100	100	100
Reaction time (min)	0	525	255	165	0	495	210	150

* from mass balance

Conclusion

The thermal pyrolysis and catalytic pyrolysis using spent FCC catalyst were investigated at various reaction temperatures. The results revealed that the thermal pyrolysis process at 450 ºC provided the maximum pyrolysis oil yield of 84.21 wt.%, which was accompanied by 37.00% naphtha, 18.60%

kerosene, 37.40% diesel, and 7.00% long residue. In a while, the catalytic pyrolysis process at 450 ºC provided the maximum pyrolysis oil yield of 70.12 wt.%, which consisted of 39.90% naphtha, 17.10% kerosene, 35.40% diesel, and 7.60% long residue. Pyrolysis is an alternative method for disposing of plastic waste on Samui Island by converting it into more valuable fuels.

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