Co-Pyrolysis technique between Used Lubricant Oil and HDPE by Activated Zeolite Catalyst

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Abstract

This research studied the optimum temperature for activating zeolite to use as a catalyst in the process of co-pyrolysis of used engine oil and high density polyethylene (HDPE) to offer diesel oil. Pyrolysis temperatures in range of 400-430 °C with catalyst of 0.5 % by weight of reactant and used engine oil per HDPE of the ratio of 100:0 by weight were performed. Zeolite was activated at 200 300 and 400°C. It was found that the optimized activated temperature at 400 °C provided the highest pyrolysis oil of 73.80 wt% while flash point temperature was lower than the standard of Department of Energy Business. Co-pyrolysis in ratio of oil:HDPE of 75:25, 50:50, 40:60, 25:75 and 0:100 by weight were studied. Experimental results showed that only the ratio of 50:50 to oil pyrolysis the qualifying standard diesel, such as flash point of 61.5 °C, specific gravity of 0.820, viscosity of 2.60 cSt, color of 3.0 and distillation of 90% recovered at 250.5 °C. The analysis of component of hydrocarbon by GC-MS of co-pyrolysis oil at the ratio of 50:50 showed the maximum linear paraffin lower than C24 (C<24) and subsequent double bonds contained hydrocarbon compounds.

Keywords: Co-pyrolysis, Lubricant Oil, High Density Polyethylene, Zeolite

1. Introduction

Plastics wastes have been continuously increasing according to their effective utilizations. The main alternatives methods of waste treatment employed today are incineration and landfill deposition for plastic wastes. However, these are far from optimal treatment options, because they can raise environmental issues, like toxic and greenhouse gas emissions, etc. Besides, their organic content is washed, otherwise, valuable in several applications. One of the benefit ways of the energetic and organic value of these wastes is pyrolysis. Most of plastic wastes from packaging such as bottle, shopping bags, etc., Polyethylene is the highest composition in municipal solid wastes, MSW. Used lubricant oils are one of the principal wastes of automobile sector. Environmental regulations require the collection of this oil, since their uncontrolled disposal may greatly hazard to underground and surface raw water. The alternative recycling processes seems to be economically uncompetitive, and only 20% of the collected oil are re-refined in Thailand. The destination of wastes oil is, depending on the country, incineration and supervised landfill.

Thallada Bhaskar et al. [1] reported thermal and catalytic treatment of waste lubricant oil with silica, silica-alumina, and alumina supported iron oxide catalysts performed at 400 °C at atmospheric pressure, Fe/SiO_2 catalyst decreased the sulphur content from 1640 to 90 ppm and produced low molecular weight hydrocarbons by cracking the high molecular weight hydrocarbons. Su Shiung Lam et al. [2] treated automotive engine oil using microwave-induced pyrolysis process, the results showed both fresh and wastes automotive oil are mostly composed of linear and branched paraffin (>85.8%), making them suitable candidates for pyrolysis, where the long-chained organic compounds are capable of being converted into valuable compounds.

Co-pyrolysis techniques have received much attention in recent years because these might allow the

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reduction of volume of waste, the recovery of chemicals and the replacement of fossil fuels. The thermal co-processing treatment methods could be environmentally friendly ways for the transformation of used engine oil and plastic waste into valuable products such as chemicals or fuels. [3]. Salepcioglu et al. [4] co-pyrolysed oil shale and LDPE and showed the increase in gas yield as the temperature of pyrolysis was increased which was attributed to gas phase cracking reactions to yield increased hydrocarbons. Additionally, it can be seen that gaseous n-paraffins and 1-olefins constitute the highest portion of the pyrolysis products. As temperature increases, the amounts of gases products increase which results as an increase in aliphatic hydrocarbon recovery.

The aim of this work, the co-pyrolysis technique of used lubricant oil with HDPE waste was studied for the optimal temperature to activated zeolite catalyst that produces liquid products. The influence of the ratio of oil:HDPE on the product yield and qualities were investigated in order to determine the optimum pyrolytic oil.

2. Materials and Methods

2.1 Materials and samples preparation

The sample of waste lubricant oil was unspecified origin. The sample of high density polyethylene (HDPE) waste were collected from drinking water bottles, its particle size was 5 mm.

2.2 Pyrolysis experiments

- Effect of Temperature activating the catalyst.

Pyrolysis experiments were performed in a 1 liter unstirred batch reactor, with atmospheric pressure of nitrogen. The 350 g of wasted oil were placed in the reactor, it was heated from room temperature to a final temperature of 430 ºC for 6 hours using 0.5 wt. % of zeolite catalyst. The catalyst was activated in a furnace to temperature of 200 ºC left for 30 minutes. The experiments were repeated by changing the catalyst activating temperature 200 ºC to 300 ºC and 400 ºC respectively. The surface characteristic by Scanning Electron Microscopy (SEM), LEO model 1450 VP LEO of each activated catalyst was investigated.

- Proportion of waste lubricant oil and HDPE

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. The accumulation of liquid product had stopped and gases products were no longer observed in the system. The reactor was visually inspected to ensure that the reaction was fully completed. The yield of solid product was determined by measurement of the weight change in the reactor, the yield of liquid product was determined by measuring the weight increase in the collected vessels. The yield of gaseous product was determined by mass balance and assumed that whatever mass of added sample not accounted for by the liquid and solid product measurements had left the system in gaseous form.

- Product analysis

The pyrolytic oils were analyzed by gas chromatography-mass spectroscopy (GC-MS) by HP-5 column, length 30 m., diameter 0.25 mm. split 10:1, flowrate 0.9 ml/min oven temperature 170 ºC until 320 ºC (10 ºC/min) used to identify their chemical composition. The other properties were analyzed based on ASTM methods as shown in Table 1.

Table 1. Analyzed ASTM methods

Properties	Standard method	Apparatus
Flash point °C	ASTM D93	Pensky Martens, model HFP 380
Viscosity @40°C	ASTM D445	Tomson, model Tv 2500
Color	ASTM D1500-96	Lovibond, model Camparator 3000 series
Specific gravity	ASTM D1298	Glass hydrometer
Distillation	ASTM D86	Tanaka, model AD-6

3. Results and Discussion

3.1 The optimum of activated temperature

After pyrolysis of waste lubricant oil, liquid product yields (oil) are presented in table 2. The results showed oil yield highly depending on activated temperature. At the highest activated temperature examined of 400 °C, the oil yield was high (73.8 wt%). For the sample of non-catalyst and catalyst, the oil yield slightly increased from non-catalyst when catalyst was used. While the oil yield was increased when activated catalyst was used. In other clockwise the solid yield were decreased when activated temperature increased. Comparing crystalline structures of zeolite which were investigated by SEM was shown in Figure 1. After zeolite was activated in the furnace at high temperature, the surface site was identified to be roughness and more surface area.

Table 3 shows the results of oil properties analysis obtained from waste lubricant oil pyrolysis in difference activated temperature. All samples showed low flash point temperature than the standard of diesel oil. Other properties (specific gravity, color, viscosity, and distillation) were on the diesel standard. The relationship between activated temperature and viscosity were investigated, viscosity of oil were decreased at high activated temperature. If distillation (90%recovered) of pyrolysis oil is more than 357 ˚C (standard of diesel oil) were indicated heavy hydrocarbon composition of product oil. The combustion of diesel engine was produced too much smoke. However, the oils (yields) from waste lubricant oil pyrolysis were low flash point comparing to of Department of Energy Business standard (<52 °C). The oil products of HDPE pyrolysis have high flash point temperature (about 65 °C) [5]. Thus, to understand the chemical reactions which could have taken place during the co-pyrolysis of waste lubricant oil with HDPE, the characterization of the liquid products obtained has been carried out in the next section.

3.2. Effect of different ratio of oil with HDPE

Six different ratio 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 430 ˚C during 6 hours. Table 4 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).

3.3 Compound of pyrolysis oil

Four ratios of oil and HDPE (types of oil products) were selected for chemical compositions analysis by GC-MS as shown in table 5. For comparison purpose, peaks were categorized into five groups: linear paraffins lower than C_{24}, linear and branched paraffins higher than C_{24}, compounds with double bounds, cyclic compounds (aliphatic hydrocarbons with cyclic structure) and aromatic compounds (eg. Benzene derivatives and PAHs) As shown in Table 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.

Table 2. Products yield of different activated temperature

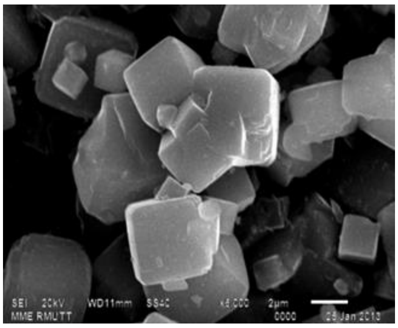
Products	Yield wt%				
	Non-catalyst	Catalyst 0.5 wt%	Activated catalyst 0.5 wt%		
			200°C	300°C	400°C
Oil	64.74	65.48	69.69	69.97	73.80
Solid	17.54	17.84	15.24	16.00	12.45
Gases	17.72	16.68	15.07	14.03	13.75

Table 3. Comparison of properties of oil yield with the diesel standard

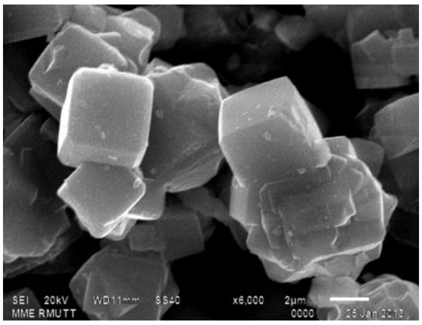
Properties	Activated Temperature			Non-catalyst	Catalyst 0.5 wt%	Diesel Standard
	200°C	300°C	400°C			
Flash point (°C)	36	33	33	31	29	>52.0
Specific gravity	0.82	0.82	0.82	0.82	0.82	0.81-0.87
Color	7.0	7.0	7.0	7.0	7.0	<7.5
Viscosity (cSt) @40°C	3.42	3.40	2.94	3.47	2.72	1.80-4.10
Distillation (°C) @90% (recovered)	264.0	251.7	297.4	374	289	<357°C

Table 4. Properties of co-pyrolysis products.

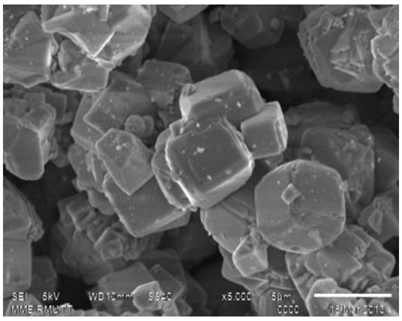
Properties	Ratio of Oil:HDPE						Diesel Standard
	100:0	75:25	50:50	40:60	25:75	0:100	
Flash point (°C)	32.5	33.0	61.5	31.5	31.5	65.5	>52 ˚C
Viscosity (cSt) @40°C	1.95	2.50	2.60	2.20	2.10	2.40	1.80-4.10
Specific gravity	0.82	0.80	0.82	0.78	0.78	0.79	0.81-0.87
Distillation ˚C @90% (recovered)	297	268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



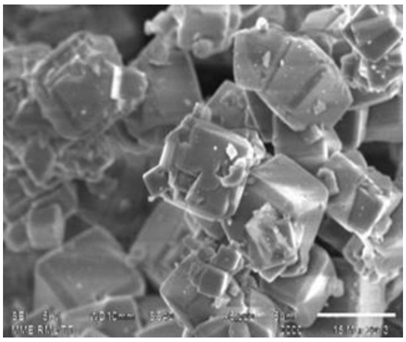
(a) before activated



(b) activated at 200 ºC



(c) activated at 300 ºC



(d) activated at 400 ºC

Figure 1. The crystalline structure of zeolite: (a) before activated, (b) activated at 200 ºC (c) activated at 300 ºC and (d) activated at 400 ºC

Table 5. Compounds of different of co-pyrolysis.

Ratio of Oil : HDPE	Compound (%)				
	Linear paraffins < C_{24}	Linear and branched paraffins > C_{24}	Double bonds compounds	Cyclic compounds	Aromatic compounds
100:0	72.888	14.174	11.988	0.949	-
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	-

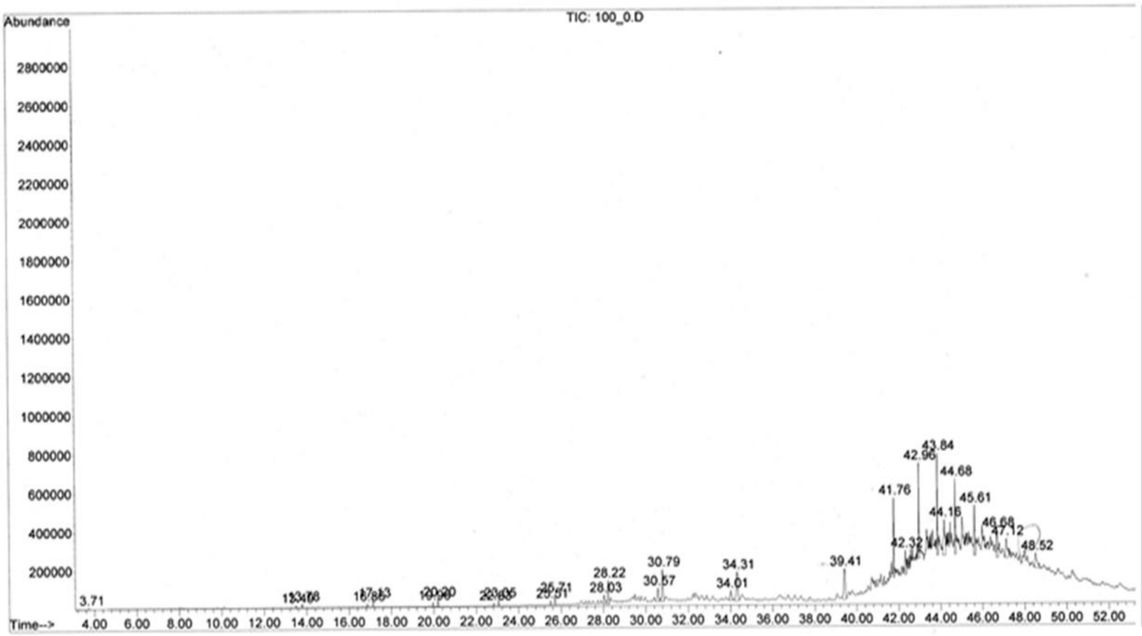


Figure 2. Hydrocarbon analysis of co-pyrolytic oil at oil:HDPE ratio 100:0 by weight

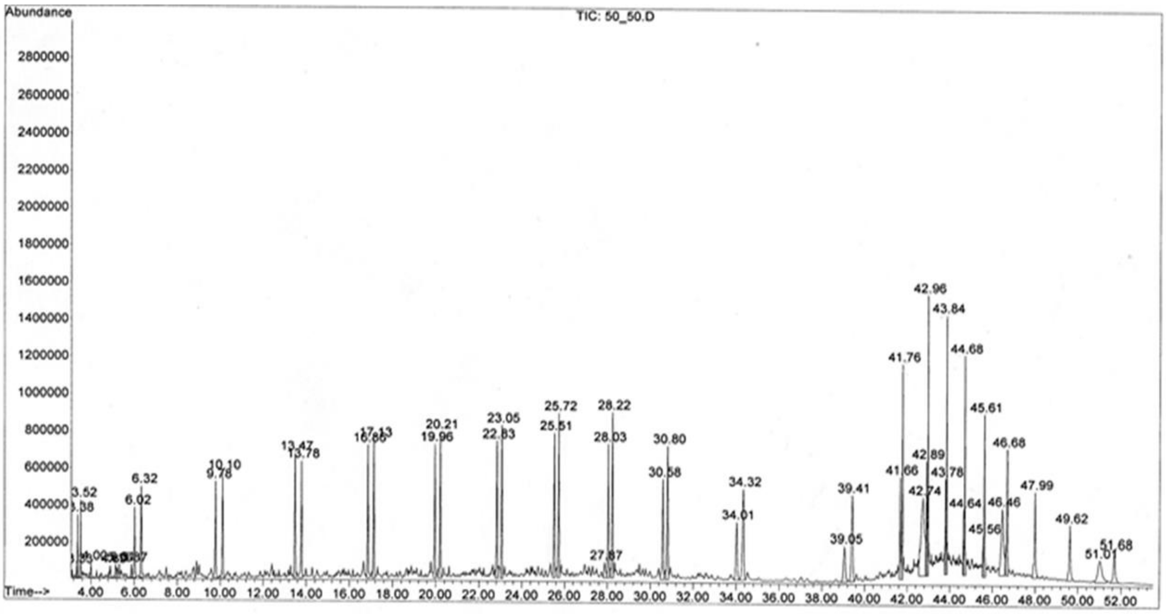


Figure 3. Hydrocarbon analysis of co-pyrolytic oil at oil:HDPE ratio 50:50 by weight

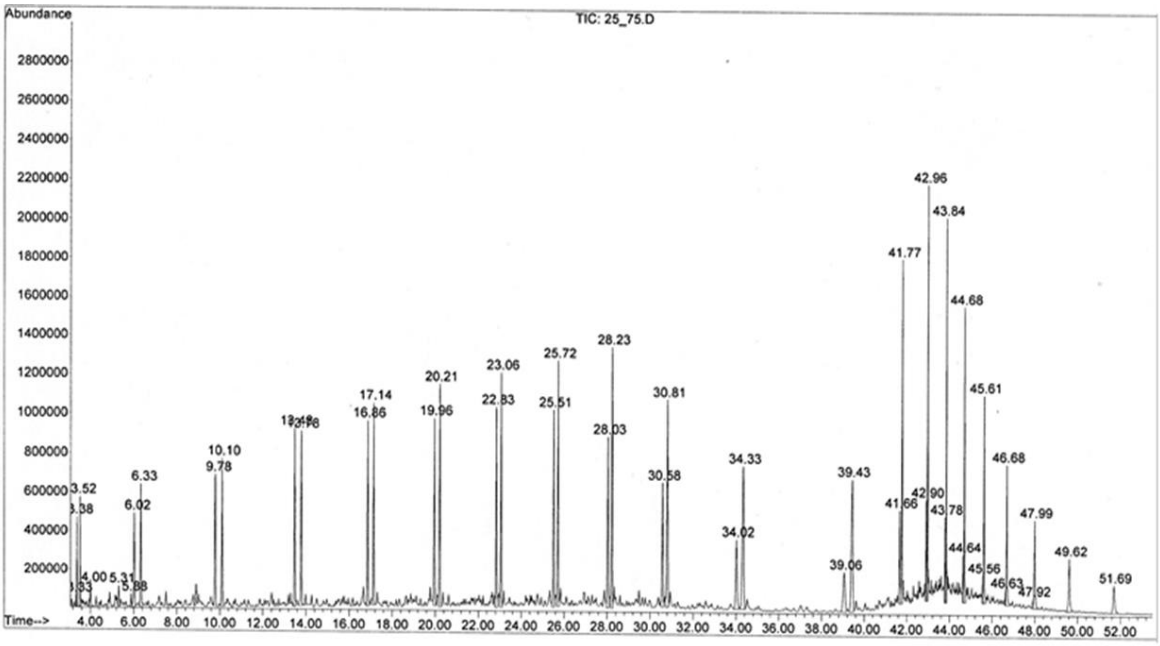


Figure 4. Hydrocarbon analysis of co-pyrolytic oil at oil:HDPE ratio 25:75 by weight

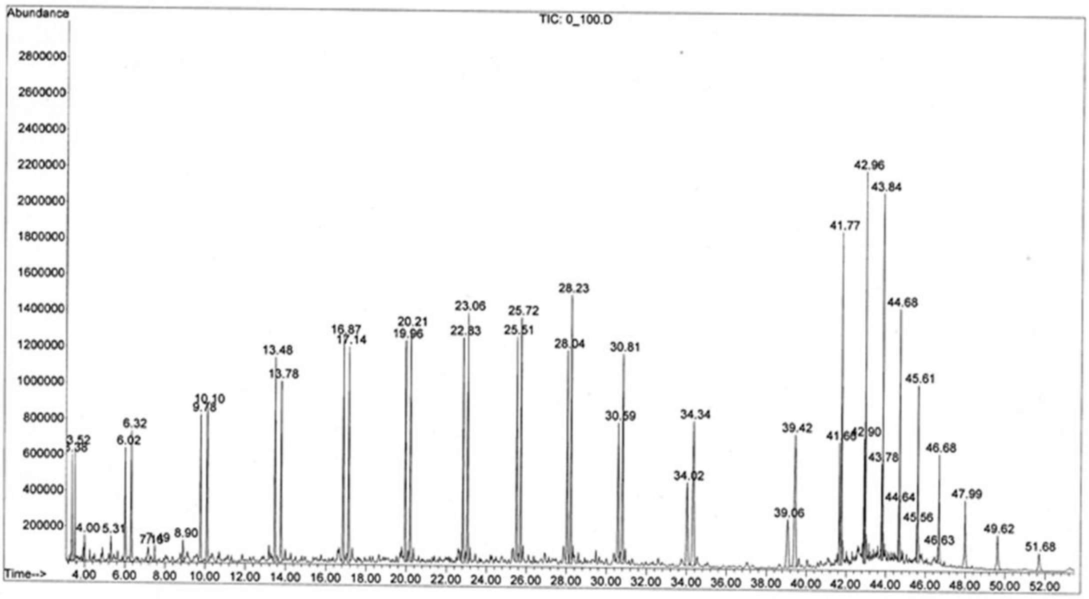


Figure 5. Hydrocarbon analysis of co-pyrolytic oil at oil:HDPE ratio 0:100 by weight

4. Conclusion

In this paper, the co-pyrolysis of waste lubricant oil and HDPE was investigated for the optimum activated temperature and ratio of waste oil:HDPE. Zeolite was optimized at activated temperature of 400 °C and provided the highest pyrolysis oil while flash point temperature was unsatisfied according to the standard. The analytical component of hydrocarbon by GC-MS of co-pyrolysis oil at ratio of 50:50 by weight had the maximum linear paraffin of lower than C_{24} (C<24) and subsequent by hydrocarbon compound with double bonds. 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).

5. Acknowledgement

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6. References

[1] Bhaskar T., Uddin M.A., Muto A. and Sakata Y., 2004. *Recycling of waste lubricant oil into chemical feedstock or fuel oil over supported iron oxide catalysts.* **Fuel**, 84:9-15.

[2] Lam S.S., Russell A.D., and Chase H.A., 2010. *Microwave pyrolysis, a novel process for recycling waste automotive engine oil.* **Energy**, 35:2985-2991.

[3] Aboulkas A., Makayssi T., Harfi K.E., Nadifiyine M., and Benchanaa M., 2012. *Co-pyrolysis of oil shale and High density polyethylene: Structural characterization of the oil*. **Fuel Processing Technology**, 96:203-208.

[4] Salepcioglu, T.Gungoren, M. Sert, S. Erdem, M. SagLam, M.Yuksel, L.Ballice, 2008.Classification of volatile product sevolved at fast co-pyrolysis of goynuk oilshale with low density polyethylene,, Oil Shale, 25: 335-347.

[5] Buddee S., Aimlamay N., and Phetyim N., 2009. Production of fuel oil from plastic wastes by pyrolysis process. Department of Chemical and Materials Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi.