

# CRACKING OF USED VEGETABLE OIL MIXED WITH POLYPROPYLENE WASTE IN THE PRESENCE OF ACTIVATED CARBON

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## Abstract

With respect to high energy demand and increasing price of fossil fuels, alternative energy is a concerned issue worldwide. Waste cooking oils and plastic wastes are attractive as starting materials for value creation due to their high existing volumes and cost saving from waste treatment. Therefore, in this work, liquid fuel was synthesized by cracking of used vegetable oil (UVO) mixed with polypropylene waste (PP) in the presence of activated carbon from coconut shell. The reactions were studied at a constant hydrogen pressure of 0.1 MPa in a batch reactor. The weight ratios of used vegetable oil and polypropylene waste were varied at 30 : 70, 50 : 50 and 70 : 30 with activated carbon to raw materials ratios of 2.5 and 5 wt% at the reaction temperature of 390 and 430°C, and reaction time of 30 and 60 mins. The amounts of gas, liquid and solid fractions were analyzed. The highest yield of total liquid hydrocarbon product was attained at a ratio of used vegetable oil to polypropylene waste of 30 : 70 wt% with activated carbon to raw materials ratios of 2.5 wt%, reaction temperature of 430°C and reaction time of 30 mins. Under these conditions, gas, liquid and solid fractions of 19.56, 79.69 and 0.75 wt% were observed. The distribution of oil fractions in liquid product was analyzed by the simulated distillation gas chromatography based on ASTM D2887, which is the standard test method for the boiling-range distribution of petroleum fractions. It was comprised of naphtha, kerosene, light gas oils, heavy gas oils and long residue of 33.20, 14.62, 19.72, 2.49 and 9.66 wt%, respectively.

**Keywords:** Activated carbon, Cracking, Polypropylene waste, Used vegetable oil

## Introduction

Renewable energy and alternative energy are choices of sustainable energy resources to compensate the increasing demand of fossil fuels and solve intense energy crisis. A number of research works involving solar energy, wind energy, and pyrolysis of biomass were undertaken [1-6]. The review papers by Bridgwater [4-6] noted that biomass had high potential to be converted to liquid fuels referred to as bio-oils and therefore they are valuable chemical feedstocks. Biomass includes natural and derived hydrocarbon materials varying from woody and herbaceous biomass, municipal solid wastes, industrial wastes, food processing and agricultural residues [3]. Pyrolysis or thermal cracking has significant advantages such as a low operating cost and various hydrocarbon products, e.g., naphtha and gas oils. Thermal cracking and catalytic cracking of vegetable oils, animal fats and plastic wastes to alternative petroleum-based fuels were studied extensively [7-9]. The pyrolysis of vegetable oils in the presence of catalyst is more common than direct thermal cracking. Thermal cracking with

catalyst reduces activation energy of the reaction. It is worth to note that waste oils or used cooking oils are more economic in liquid fuel synthesis than edible oils. Typical temperature of the pyrolysis of used cooking oil ranges between 400-420°C. The obtained pyrolysis oil contained C<sub>5</sub>-C<sub>17</sub> hydrocarbons including paraffins, olefins and aromatics [7]. Research in the area of vegetable oil pyrolysis is not as ample as the area of biodiesel by transesterification reaction using strong base catalysts such as sodium or potassium hydroxide [10].

Apart from used cooking oils, abundant plastic wastes draw extreme interest as they can be cracked to lower molecular hydrocarbons for gasoline [11] Particularly, if a suitable catalyst is selected, it increases favorable structure of the products [11-13]. For example, Uemichi et al. [13] reported that aromatics were increased but branched alkanes were decreased when platinum impregnated on activated carbon and on silica alumina were used in the degradation of polyethylene at 526°C. Several papers showed that fuel-like hydrocarbons could be obtained by thermal and catalytic cracking [7,9,11,14].

In short, the purpose of this investigation was cracking of used vegetable oil mixed with polypropylene waste as raw materials in the presence of activated carbon from coconut shell at a constant hydrogen pressure of 0.1 MPa in a batch reactor. The compositions of used vegetable oil and polypropylene waste were varied at the weight ratios of 30 : 70, 50 : 50 and 70 : 30 using activated carbon to raw materials ratios from 2.5 to 5 wt% at the reaction temperature of 390 and 430°C, and reaction time of 30 and 60 mins.

## Theoretical

### Thermal and Catalytic Cracking

Pyrolysis process or thermal cracking is thermal decomposition of high molecular hydrocarbon into low molecular hydrocarbon. The final products are similar to naphtha and diesel fractions in conventional petroleum refining. Catalytic cracking and hydrocracking are complex because they include hydrogenation of aromatic hydrocarbons, opening of naphthenic rings and isomerization, which increases product's octane number [15]. In other words, hydrocracking reduces polymerization of heavy hydrocarbon into coke by converting them to light hydrocarbon products. Thermal and catalytic mechanisms of vegetable oil have been proposed [7]:

- Vegetable oil (e.g., Canola oil) → Heavy oxygenated C<sub>x</sub>H<sub>y</sub> (thermal cracking)
- Heavy oxygenated C<sub>x</sub>H<sub>y</sub> → Heavy C<sub>x</sub>H<sub>y</sub> + H<sub>2</sub>O + CO<sub>2</sub> + CO (thermal and catalytic cracking)
- Heavy C<sub>x</sub>H<sub>y</sub> → Paraffins + Olefins (short and long chains) (thermal and catalytic cracking)
- Light olefins ⇌ C<sub>2</sub> – C<sub>10</sub> olefins (catalytic cracking)
- C<sub>2</sub> – C<sub>10</sub> olefins ⇌ Aromatic C<sub>x</sub>H<sub>y</sub> + Aliphatic C<sub>x</sub>H<sub>y</sub> (catalytic cracking)
- Vegetable oil (e.g., Canola oil) → Coke (thermal cracking)
- n(Aromatic) → Coke (catalytic cracking)

In case of plastic pyrolysis, main products consist of paraffins, olefins and higher-boiling-point hydrocarbon products, while the products of catalytic cracking consist of more iso-alkanes and aromatics (desirable gasoline-range hydrocabons) [11]. Four types of mechanisms of plastics pyrolysis have been reported by Cullis and Hirschler [16].

- End-chain scission: The polymer is broken up from the end groups successively yielding the corresponding monomers.
- Random-chain scission: Polymer chain is broken up randomly into fragments of uneven length.

- Chain-stripping: Elimination of reactive substitutes or side groups on the polymer chain, leading to the evolution of a cracking product on one hand, and a charring polymer chain on the other.
- Cross-linking: Formation of a chain network, which often occurs for thermosetting polymers when heated.

Decomposition mechanism of polypropylene is mainly by random-chain scission which monomeric yield is less than 1% of volatile product [11].

### **Activated Carbon**

Activated carbon has a microcrystalline structure with micropores, mesopores and macropores, and can be produced from coconut shell, coal or wood by carbonization process. Micropore diameter is less than 2 nm with pore volume of 0.15 to 0.70 cm<sup>3</sup>/g. Its surface area is about 95% of the total surface area. Mesopore diameter ranges from 2 to 50 nm with pore volume of 0.1 to 0.2 cm<sup>3</sup>/g. The surface area does not exceed 5% of the surface area. Macropore diameter is larger than 50 nm with pore volume of 0.2 to 0.4 cm<sup>3</sup>/g and the surface area of this structure does not exceed 0.5 m<sup>2</sup>/g. Activated carbon is applied in several processes such as industrial wastewater treatment, and can be used as a catalyst, catalyst support or adsorbent [17].

## **Experimental**

### **Materials**

Used vegetable oil (UVO) and saline-solution bag polypropylene waste (PP) were used as raw materials. Activated carbon with a diameter of 0.60-0.85 mm and internal surface area of 850-2,000 m<sup>2</sup>/g was supplied by Jacobi Carbons. Before the experiments, degradation of used vegetable oil and polypropylene waste were characterized by thermogravimetry (TG).

### **Pyrolysis**

The reactor in this work can withstand the temperature and pressure no higher than 480° C and 10 MPa. Raw materials (UVO mixed with PP) were preheated at 300°C for 10 mins to start the melting of polypropylene waste by an electrical heater. Different weight ratios of UVO : PP of 30 : 70, 50 : 50 and 70 : 30, with total weight of 10 grams were pyrolyzed at 390 and 430°C and reaction time of 30 and 60 mins at a constant hydrogen pressure of 0.1 MPa in the presence of activated carbon to raw materials (AC : RM) of 2.5 and 5 wt% in a 70-ml batch reactor (Fig. 1). Two experiments were repeated to examine each experimental condition and the results were averaged. For each ratio of UVO : PP, 4 test conditions were studied. In case of first and second test conditions, AC : RM were varied at 2.5 and 5 wt% at 390°C and 30 mins. Accordingly, the AC : RM that produced high yield of liquid fraction (pyrolysis oil) was selected and fixed for the following test conditions by changing the temperature to 430°C and varying reaction time to 30 and 60 mins. Then, the weight fractions of gas, liquid and solid were analyzed. The distribution of oil fractions in liquid fraction was analyzed by the simulated distillation gas chromatography based on ASTM D2887, which is the standard test method for the boiling-range distribution of petroleum fractions [18]. The boiling ranges of oil fractions are shown in Table 1.

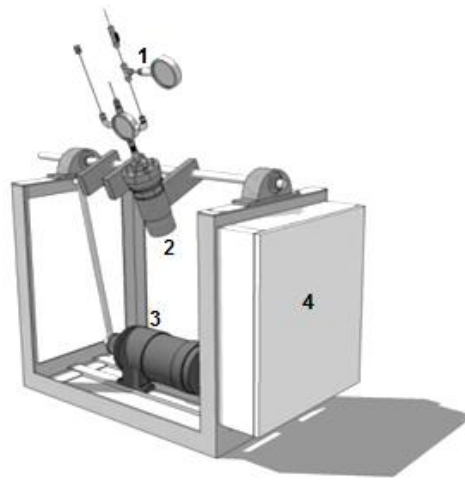


Figure 1. Sketch of the experimental kit: 1. pressure gauge, 2. reactor, 3. reactor-movement machine and 4. temperature controller box

**Table 1. Boiling Ranges of Oil Fractions [18]**

Boiling Ranges (°C)	Fractions
IBP – 200	Naphtha (C <sub>5</sub> – C <sub>11</sub> )
200 – 250	Kerosene (C <sub>11</sub> – C <sub>14</sub> )
250 – 350	Light gas oils (C <sub>14</sub> – C <sub>20</sub> )
350 – 370	Heavy gas oils (C <sub>20</sub> – C <sub>25</sub> )
370 – FBP	Long residue (> C <sub>25</sub> )

## Results and Discussion

Figure 2 indicates the degradation temperature of used vegetable oil and polypropylene waste. As shown, UVO and PP degraded approximately from 350-400°C. Therefore, in this work, the cracking temperature of UVO mixed with PP started from 390°C.

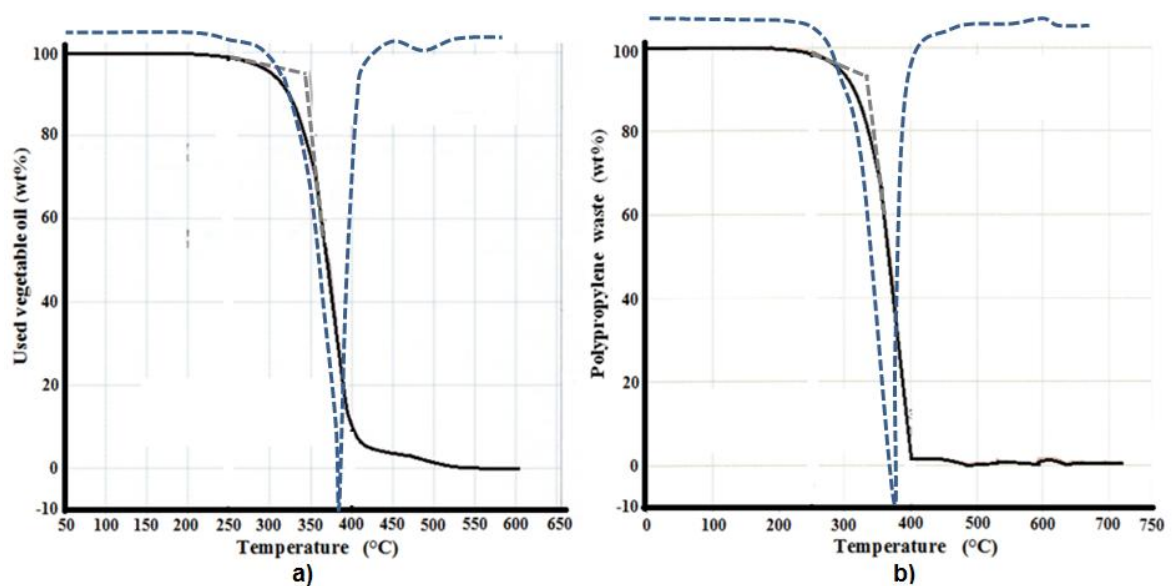


Figure 2. Degradation characterization by thermogravimetric analyzer  
(a) used vegetable oil (b) polypropylene waste

### Effect of The Ratio of Activated Carbon to Raw Materials (AC : RM) on Pyrolysis Oil

From Figure 3, compared to AC : RM of 5 wt%, AC : RM of 2.5 wt% obtained higher average yield of pyrolysis oil at every ratio of UVO : PP due to more amounts of raw materials, and the effect of polymerization of aromatics that changed pyrolysis oil to solid or coke [7]. Thus, AC : RM of 2.5 wt% was fixed for the subsequent test conditions.

In addition, the maximum pyrolysis oil of 73.95 wt% was observed when UVO and PP of 70 : 30 wt% was used.

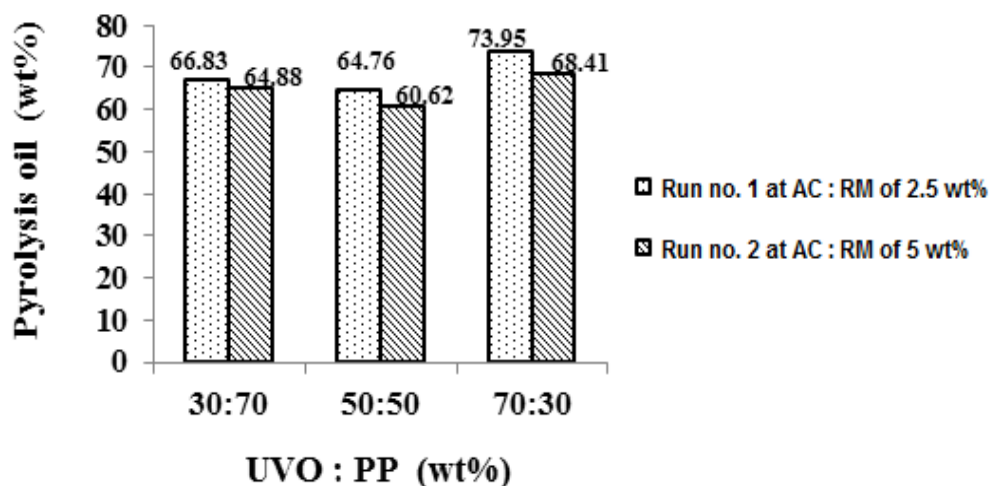


Figure 3. Effect of the ratio of activated carbon to raw materials on pyrolysis oil at 390°C and 30 mins

### Effect of Reaction Temperature and Time on Pyrolysis Oil

For every ratio of UVO : PP at higher temperature of 430°C, more amount of pyrolysis oil was acquired compared to that from 390°C, as shown in Figure 4. This is because PP degrades completely and solid continues cracking to pyrolysis oil and gas at higher temperature. Therefore, more pyrolysis oil was obtained when the ratio of polypropylene waste was higher than used vegetable oil (UVO : PP = 30 : 70 wt%).

The effect of reaction time is shown in Figure 5. At the same ratio of UVO : PP, AC : RM ratio of 2.5 wt%, and temperature of 430°C, less pyrolysis oil was observed at 60 mins because longer reaction time resulted in further cracking of UVO and PP to gas fraction. However, more pyrolysis oil was obtained at UVO : PP = 30 : 70 wt% same as stated in Figure 4.

From this work, the highest amount of pyrolysis oil of about 80 wt% was achieved at the following conditions: UVO : PP = 30 : 70 wt%, AC : RM = 2.5 wt%, 430°C and 30 mins. However, because the viscosity and color of the pyrolysis oil depend primarily on the reaction temperature and time, favorable viscosity and color (light color) were obtained at 430°C and 60 mins.

According to the results by other researchers, e.g., Dandik et al. [19] who worked on pyrolysis of used sunflower oil by using sodium carbonate to 10 wt% used sunflower oil in a 180-mm packed column at 420°C and 180 mins, they obtained 47.27 wt% of pyrolysis oil containing 36.42 wt% of naphtha. Kim et al. [20] gained 33.3 wt% of pyrolysis oil on pyrolysis of polypropylene in the presence of HZSM-5 at 400°C and 120 mins in a semi-

batch reactor. As per the aforementioned results, we achieved more pyrolysis oil in a shorter reaction time from waste raw materials.

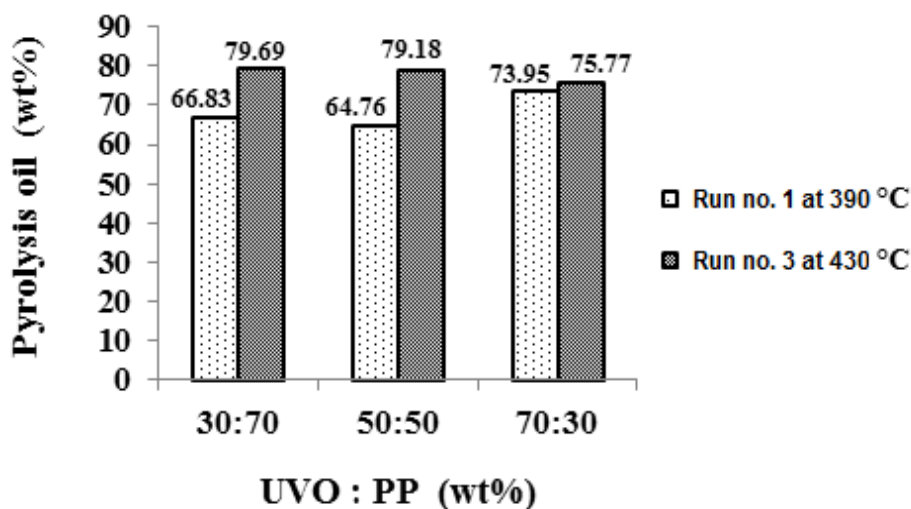


Figure 4. Effects of reaction temperature and UVO : PP on pyrolysis oil at 30 mins using AC : RM of 2.5 wt%

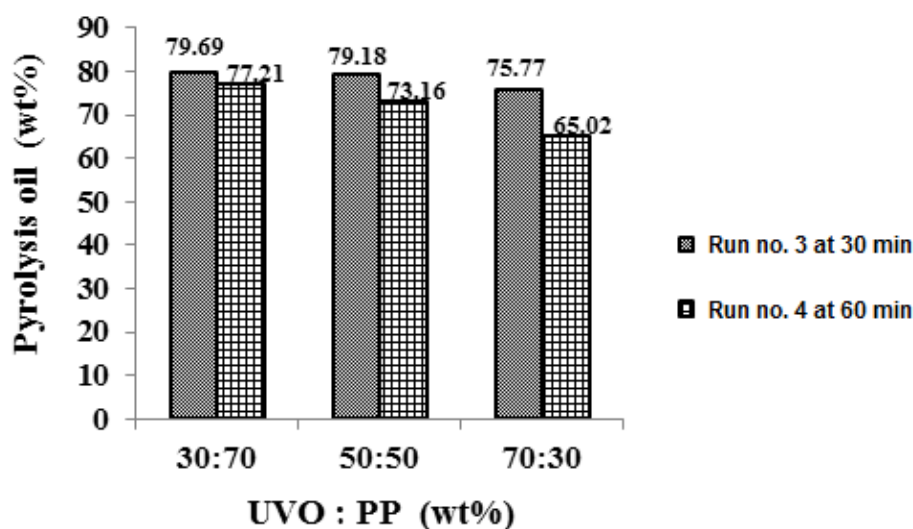


Figure 5. Effects of reaction time and UVO : PP on pyrolysis oil at 430°C using AC : RM of 2.5 wt%

### Yields and Distribution of Oil Fractions in Pyrolysis Oil

Yields in terms of weight fractions of gas, liquid and solid obtained in this work were analyzed and shown in Table 2. A small amount of solid increased with AC : RM ratio of 5 wt%. However, when the reaction temperature increased to 430°C, it was obvious that solid cracked drastically, and therefore the amounts of pyrolysis oil and gas increased significantly. For every ratio of UVO : PP (30 : 70, 50 : 50 and 70 : 30 wt%) by using AC : RM of 2.5 wt% and the reaction temperature of 430°C but longer reaction time, the amount of pyrolysis oil decreased because it continued cracking to gas and solid. For all UVO : PP ratios, the maximum pyrolysis oil and the minimum solid were obtained at AC : RM of 2.5 wt%, 430°C and 30 mins.

**Table 2. Yields from the Experiments**

UVO : PP <sup>1</sup> (wt%)	Run no.	AC : RM <sup>2</sup> (wt%)	Temperature (°C)	Time (mins)	Yields (wt%)		
					Gas	Liquid	Solid
30 : 70	1	2.5	390	30	8.34	66.83	24.83
	2	5	390	30	8.59	64.88	26.53
	3	2.5	430	30	19.56	79.69	0.75
	4	2.5	430	60	21.74	77.21	1.05
50 : 50	1	2.5	390	30	6.94	64.76	28.31
	2	5	390	30	6.59	60.62	32.79
	3	2.5	430	30	18.87	79.18	1.95
	4	2.5	430	60	24.39	73.16	2.45
70 : 30	1	2.5	390	30	8.35	73.95	17.70
	2	5	390	30	9.03	68.41	22.56
	3	2.5	430	30	19.68	75.77	4.55
	4	2.5	430	60	30.29	65.02	4.70

1 UVO : PP = used vegetable oil : polypropylene waste

2 AC : RM = activated carbon : raw materials

Table 3 shows the distribution of oil fractions in pyrolysis oil analyzed by the simulated distillation gas chromatography based on ASTM D2887. It is likely that cracking of used vegetable oil mixed with polypropylene waste in the presence of activated carbon can be a preference for alternative fuels. The highest amount of naphtha fraction of about 33.20 wt% was obtained at UVO : PP of 30 : 70 wt%, AC : RM of 2.5 wt%, reaction temperature of 430°C and reaction time of 30 mins. The ratio of UVO and PP in raw material has an effect on product distribution. For instance, raw material with high PP (70 wt%, UVO : PP = 30 : 70 wt%) produced more amount of naphtha compared to raw materials with PP of 30 wt%.

Figure 6 concludes yields (gas, liquid and solid) from cracking reaction, and oil fractions in liquid product (pyrolysis oil) at the best experimental conditions. The desired fractions are naphtha for gasoline and gas oils for diesel oil. Their essential properties needed to be further analyzed to compare with conventional gasoline and diesel oil.

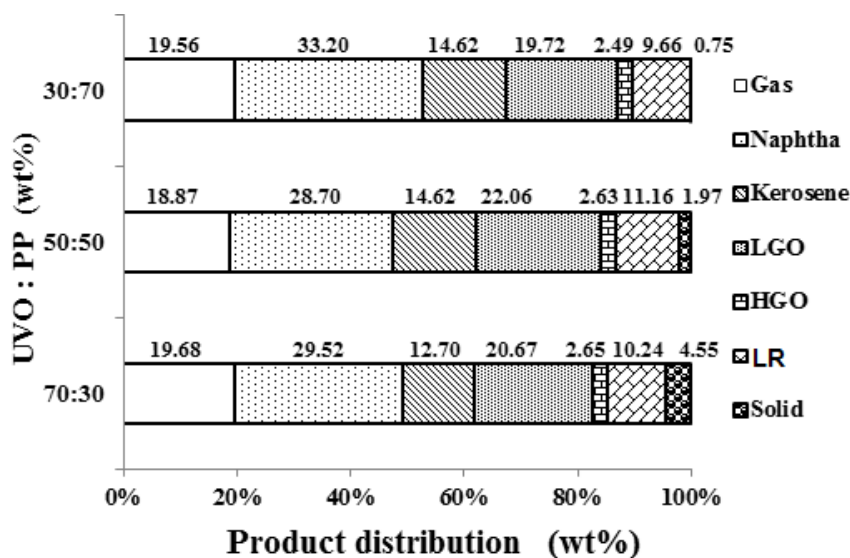


Figure 6. Yields and oil fractions in pyrolysis oil at the best experimental conditions

**Table 3. Distribution of Oil Fractions in Pyrolysis Oil at Different Weight Ratios of Raw Materials from Different Conditions (Run no. 1: AC : RM = 2.5 wt%, 390°C, 30 mins; Run no. 2: AC : RM = 5 wt%, 390°C, 30 mins; Run no. 3: AC : RM = 2.5 wt%, 430°C, 30 mins; Run no. 4: AC : RM = 2.5 wt%, 430°C, 60 mins)**

UVO : PP <sup>1</sup>	Run no.	Product distribution (wt%)				
		Naphtha	Kerosene	LGO <sup>2</sup>	HGO <sup>3</sup>	LR <sup>4</sup>
30 : 70	1	15.57	7.45	14.98	3.17	25.65
	2	12.40	7.14	14.68	3.24	27.41
	3	33.20	14.62	19.72	2.49	9.66
	4	29.05	15.05	20.17	2.41	10.52
50 : 50	1	7.04	5.91	18.86	4.21	28.74
	2	4.40	5.07	19.80	6.24	25.11
	3	28.70	14.62	22.06	2.63	11.16
	4	25.43	14.73	20.94	2.56	9.51
70 : 30	1	9.66	6.03	22.48	5.20	30.58
	2	9.18	5.57	20.94	5.05	27.67
	3	29.52	12.70	20.67	2.65	10.24
	4	22.09	12.84	19.09	2.21	8.79

1 UVO : PP = used vegetable oil : polypropylene waste

2, 3, 4 LGO = light gas oils, HGO = heavy gas oils, LR = long residue

## Conclusions

Used vegetable oil and plastic wastes are one of potential alternative energy sources. They were successfully converted to liquid fuels such as naphtha and gas oils by pyrolysis process in the presence of the catalyst such as activated carbon. The highest yield of total liquid hydrocarbon products as high as 80 wt% (consisting of naphtha (gasoline-range hydrocarbon) of 33.20 wt% and gas oils of 22.21 wt%) was attained under the hydrogen atmosphere of 0.1 MPa at the following conditions: ratio of used vegetable oil to polypropylene waste of 30:70 wt%, activated carbon to raw materials ratio of 2.5 wt%, reaction temperature of 430°C and reaction time of 30 mins. Using used vegetable oil mixed with plastic wastes as the raw material is value creation. It is likely to be economically competitive at high fossil fuel price. In addition, the reaction in a batch reactor can be easily scaled up to a continuous reactor for higher production.

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## References

- [1] R. Banos, F.M. Agugliaro, F.G. Montoya, C. Gil, A. Alcayde, and J. Gomez, "Optimization methods applied to renewable and sustainable energy : A review," *Renewable and Sustainable Energy Reviews*, Vol. 15, pp. 1753-1766, 2011.



- [2] N.L. Panwar, S.C. Kaushik, and S. Kothari, "Role of renewable energy sources in environmental protection : A review," *Renewable and Sustainable Energy Reviews*, Vol. 15, pp. 1513-1524, 2011.
- [3] S. Yaman, "Pyrolysis of biomass to produce fuels and chemical feedstocks," *Energy Conversion and Management*, Vol. 45, pp. 651-671, 2004.
- [4] A.V. Bridgewater, "Principles and practice of biomass fast pyrolysis processes for liquids," *Journal of Analytical and Applied Pyrolysis*, Vol. 51, pp. 3-22, 1999.
- [5] A.V. Bridgewater, "Renewable fuels and chemicals by thermal processing of biomass," *Chemical Engineering Journal*, Vol. 91, pp. 87-102, 2003.
- [6] A.V. Bridgewater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and Bioenergy*, Vol. 38, pp. 68-94, 2012.
- [7] K.D. Maher, and D.C. Bressler, "Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals," *Bioresource Technology*, Vol. 98, pp. 2351-2368, 2007.
- [8] J. Xu, J. Jiang, Y. Sun, and J. Chen, "Production of hydrocarbon fuels from pyrolysis of soybean oils using a basic catalyst," *Bioresource Technology*, Vol. 101, pp. 9803-9806, 2010.
- [9] E. Sannita, B. Aliakbarian, A.A. Casazza, P. Perego, and G. Busca, "Medium-temperature conversion of biomass and wastes into liquid products : A review," *Renewable and Sustainable Energy Reviews*, Vol. 16, pp. 6455-6475, 2012.
- [10] Y.C. Sharma, B. Singh, and S.N. Upadhyay, "Advancements in development and characterization of biodiesel," *Fuel*, Vol. 87, pp. 2355-2373, 2008.
- [11] A.G. Buekens, and H. Huang, "Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes," *Resources, Conservation and Recycling*, Vol. 23, pp. 163-181, 1998.
- [12] A. Angyal, N. Miskolczi, L. Bartha, and I. Valkai, "Catalytic cracking of polyethylene waste in horizontal tube reactor," *Polymer Degradation Stability*, Vol. 94, pp. 1678-1683, 2009.
- [13] Y. Uemichi, Y. Makino, and T. Kanazuka, "Degradation of polyethylene to aromatic hydrocarbons over metal-supported activated carbon catalyst," *Journal of Analytical and Applied Pyrolysis*, Vol. 14, pp. 331-344, 1989.
- [14] M. Jozef, and V. Miriam, "Catalytic and thermal cracking of selected polyolefins," *Clean Technologies and Environmental Policy*, Vol. 10, pp. 121-130, 2008.
- [15] S. Raseev, *Thermal and Catalytic Processes in Petroleum Refining*, Marcel Dekker, New York, 2003.
- [16] C.F. Cullis, and M.M. Hirschler, *The Combustion of Organic Polymers*, Clarendon Press, Oxford, 1981.
- [17] R.C. Bansal, and M. Goyal, *Activated Carbon Adsorption*, CRC Press, Florida, 2005.
- [18] M.A. Fahim, T.A. Alsahhaf, and A. Elkilani, *Fundamentals of Petroleum Refining*, Elsevier, Amsterdam, 2010.
- [19] L. Dandik, and H.A. Aksoy, "Pyrolysis of used sunflower oil in the presence of sodium carbonate by using fractionating pyrolysis reactor," *Fuel Processing Technology*, Vol. 57, pp. 81-92, 1998.
- [20] J.R. Kim, J.H. Yoon, and D.W. Park, "Catalytic recycling of the mixture of polypropylene and polystyrene," *Polymer Degradation Stability*, Vol. 76, pp. 61-67, 2002.