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Microwave Pyrolysis of C6 Non-aromatic Hydrocarbons

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Abstract. C6 non-aromatic hydrocarbons obtained from olefins plant was used as a feedstock in microwave pyrolysis. The experiment was carried out in a microwave reactor over an activated carbon, which acts as a microwave receptor. Operating temperature (from 500 to 700 ºC), controlled by power of microwave reactor, was varied to observe the consequence on the pyrolysis products. The chemical composition and product yield of the pyrolysis products (liquid oil and gas) were analyzed by using gas chromatography/mass spectrometry (GC/MS). The results indicated that microwave pyrolysis has the potential to upgrade low value hydrocarbons into high value products. The recovered liquid and gaseous pyrolysis products contained various hydrocarbons which could be used as a valuable industrial feedstock.

Keywords: Microwave, Microwave Pyrolysis, C6 Non-aromatic, Hydrocarbons.

1. Introduction

Chemical industries have rapidly grown up, especially petrochemical industry. The products derived from the petrochemical industry are generally used as a raw material for many downstream industries to supply the increasing demand for synthetic products and daily life products. Hydrocarbons such as LPG, naphtha, and condensate, are typically used as raw material in the upstream petrochemical industry where olefins products such as ethylene and propylene are produced. Pyrolysis is conventionally and widely used as a thermal conversion process to convert the hydrocarbons feed into the olefins products [1, 2]. The process, also known as thermal cracking, takes place at a high temperature in the absence of oxygen. After passing a pyrolysis chamber, heavy hydrocarbons feed will be broken down into lighter molecules. In addition to the olefins products, several mixed hydrocarbon by-products are also produced. Some of these by-products are normally separated and sold to other users at low price. Often, they are sent back to the pyrolysis chamber as a recycle stream.

Due to the strong competitiveness of petrochemical business, the utilization of by-products from the manufacture is very crucial. It is more desirable to upgrade by-products by turning them into more valuable products rather than being used as the recycle stream. Furthermore, in the conventional pyrolysis, there is large amount of energy losses during the heat transfer from a heat source to the raw material in the pyrolysis chamber. Also, the pyrolysis can promote undesired by-products. According to energy concern and recent pollution problems, novel production technologies that are more efficient, consume less energy, and able to upgrade the low-valued products have been substantially sought and developed.

Microwave pyrolysis is a relatively new technique which provides many advantages over conventional pyrolysis process. It is extremely efficient method in selective heating of materials as the energy can be transferred directly to the material [2, 3, 4]. This results in less energy consumption, process time saving and more environmental friendly. In addition, the use of microwave in hydrocarbon conversion has a high potential to produce new hydrocarbon products and also reduce unwanted side reaction that usually occurs in the conventional processes. In recent years, the use of microwave pyrolysis has been employed in the

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pyrolysis of glycerol over a carbonaceous catalyst, the microwave pyrolysis showed the higher gas fraction with an elevated content of synthesis gas compared to conventional heating (up to 81 vol. %) [5]. Moreover, the microwave pyrolysis shows the recovery of commercially valuable products (light gas and aromatic compounds) from the waste oil more than traditional pyrolysis process [6, 7]. In this paper, the study of upgrading C6 non-aromatic by-product obtained from olefins process with microwave pyrolysis over activated carbon is reported. The influence of pyrolysis temperature and power of microwave were investigated and the composition and yields of products were analyzed and presented. This work has been conducted with the aim to assess the technical feasibility of using microwave pyrolysis to upgrade by-product from olefins process.

Table 1: The constituents of C6 non-aromatic hydrocarbon

Compound name	**C6-Non-Aromatic (% wt)**
2,3-dimethylbutane	16.12
2-methyl pentane	11.65
n-Hexane	16.94
Ethyl cyclopentane	28.89
Cyclohexane	7.72
Others	18.60

2. Experiment

2.1. Materials

C6 non-aromatic mixed hydrocarbon obtained from an olefins plant was used as raw material throughout the experiments. The compositions of the raw material were shown in Table 1.

Hydrocarbons are typically poor on absorbing the microwave energy. Thus, in order to rise the temperatures in the microwave reactor chamber to a level that pyrolysis can take place, another material that can easily absorb the microwave energy should be placed inside the chamber. In this work, pellet activated carbon was used as a microwave receptor to heat up the hydrocarbon feedstock. Since activated carbon may contain some moisture content which could interact with the pyrolytic reaction, it is necessary remove the moisture inside the activated carbon by heating at 110 ºC for 20 minutes prior to the start of the experiments.

2.2. Experimental Apparatus

The microwave pyrolysis experiments were conducted on a lab scale quartz reactor and modified microwave. The system consists of modified 1,100 W household microwave oven, quartz reactor (355 mm height, 27 mm inner diameter, and 32 mm outer diameter), peristaltic pump, liquid collecting vessel, and condenser unit. In all experiments, 10 grams of pellet activated carbon was used and the flow rate of nitrogen carrier gas was set at 20 ml/min. The experimental setup was shown in Fig. 1.

2.3. Experimental Methods

Ten grams of pellet activated carbon was placed into the quartz reactor. In order to ensure an inert atmosphere during the treatments, nitrogen gas was fed into the apparatus at a flow rate 20 ml/min. A complete purge of air was ensured by washing out the system with nitrogen gas for at least 10 minute prior to the start. The pellet activated carbon was heated up to the target temperature between 500 to 700 ºC. The temperature of the sample during the experiments was monitored by means of an infrared optical pyrometer. The infrared thermometer measures surface temperature of an object. The emissivity parameter was set in the infrared thermometer for each material expected to represent the average temperature of the bulk material quite accurately. Once the target temperature was attained the reactor was left for 10 minute to ensure complete temperature equilibration. The mixed hydrocarbon sample was then injected into the quartz reactor. The gas products obtained from the reactor pass through the condenser unit where some liquid products were obtained and their compositions were analyzed by 6890/5973 GC-MS instrument (Agilent Technologies, USA) at the room temperature. The GC-MS was operated in spilt mode (1:300), using HP-5MS column. The incondensable gases pass through the condenser unit to the gas sampling point where they are collected by a gas bag for transferred into GC-MS with gas tight syringe at the room temperature. Gas samples were analyzed in spilt mode (1:50) using HP-5MS column.

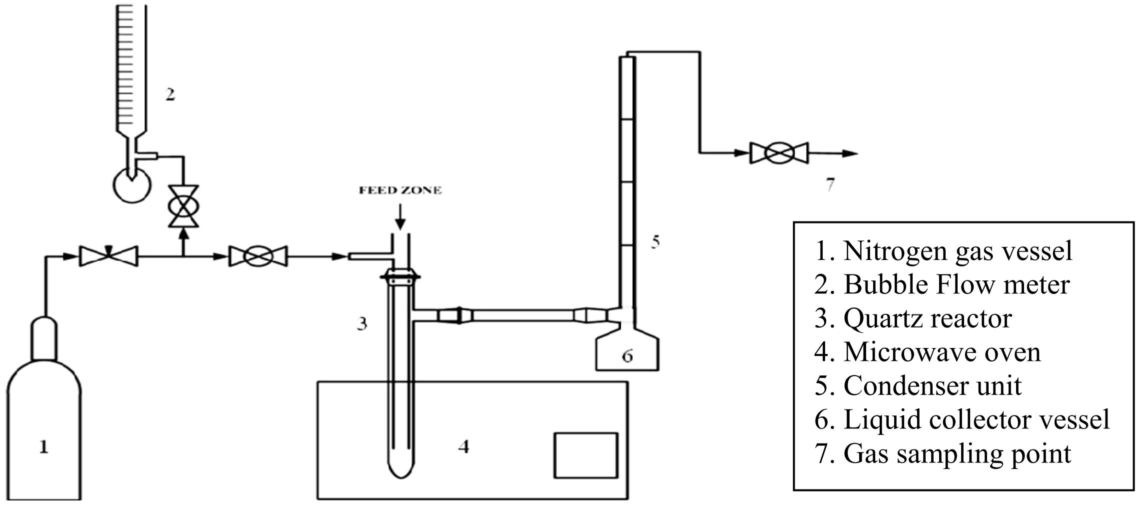

Fig. 1: Schematic layout of microwave pyrolysis system.

3. Results and Discussion

3.1. Temperature Profiles

The temperature profiles of pellet activated carbon (10 g) under microwave power of 110, 330, 550, 770 and 1100 Watts are shown in Fig. 2. It can be seen from the Fig.2 that, in the most cases, the temperature increased rapidly during the first 5 minutes and the temperatures were relatively stable after 10 minute. Also, the target operating temperatures of about 500, 600 and 700 º C were easily achieved in 10 minute under 330, 550, and 770 W, respectively. The stability and reproductivity of temperature profile were also obtained under those microwave power. After 10 minutes of reaction, there was almost no significant change in the temperature. Therefore, the experiment results obtained under microwave power of 330, 550, and 770 W for operating temperature 500,600 and 700 ºC were primarily selected.

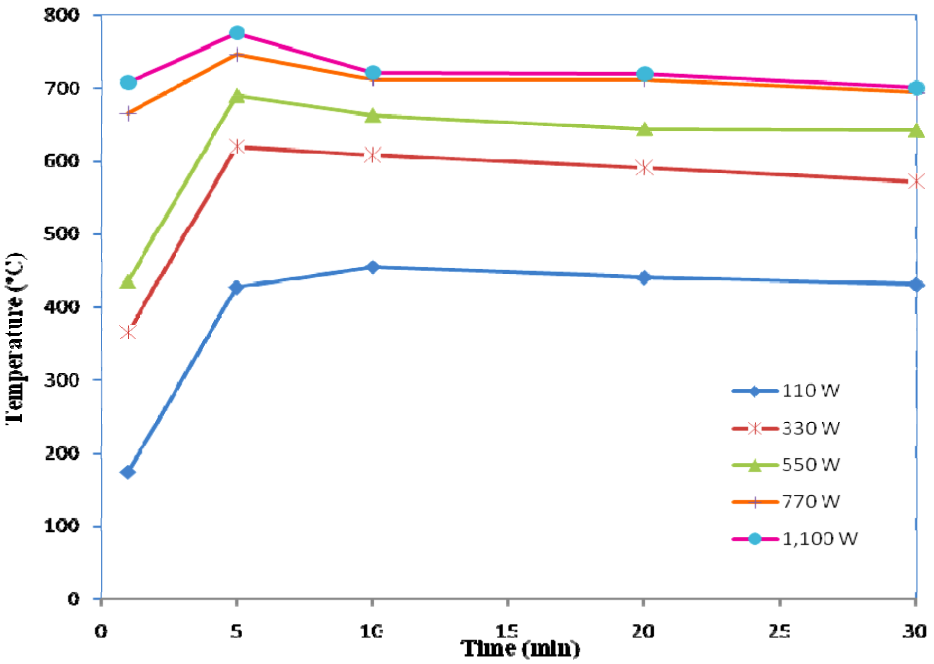

Fig. 2: The temperature profiles under different microwave power

3.2. Compositions and Yields of the Product

Table 2 demonstrates the main gaseous product obtained at different operating temperatures in the microwave pyrolysis. It is clearly seen that temperature has a great influence on the fraction of gas and liquid products. With respect to the gaseous product, some interesting compounds corresponding to C3-C6 were detected. In the lowest temperature (500 ºC), the yields of C3-C4 were found to be high when compared to other gases. The increase of operating temperature brings about lower production of C5-C6 such as pentane in the gaseous products. The resulting gaseous products represent potential high-value chemical compounds which could be used as other chemical feedstock.

Table 2: The main pyrolysis product compounds in the gases.

Chemical name	Relative proportions (% area)		
	Temperature (ºC)		
	500	600	700
1-Propene	25.09	22.47	21.76
2-Methyl-1-propane	10.38	10.49	9.08
Methylcyclopentane	2.68	5.26	3.95
Cyclohexane	0.25	0.58	-
Pentane	1.15	1.05	-
Others	9.97	13.65	11.44

In the liquid product, Table 3 shows a constituent of the main pyrolysis product in the oils obtained from the pyrolysis of the mixed hydrocarbon using the microwave oven with activated carbon as absorber. The pyrolysis oil is complex mixtures of organic compounds with wide variety of the chemical groups; for example, mono-aromatic compounds including benzene, benzene alkyl derivative; n-alkanes with number of carbons ranging from C3-C8. Methylcyclopentane is a member of the methyl derivatives of aliphatic compounds. It is one of the important benzene precursors that can react in refinery processes to form benzene. Also, polycyclic aromatic compounds (PACs) such as naphthalene can be produced in the microwave pyrolysis. Overall, it can be seen that the liquid products from the pyrolysis of mixed hydrocarbon using microwave show a good potential to be used as useful industrial feedstock.

Table 3: The main pyrolysis product compounds in the oils

Chemical name	Relative proportions (% area)		
	Temperature (ºC)		
	500	600	700
2-Methylpentane	17.78	11.37	-
Hexane	18.15	14.87	8.43
Methylcyclopentane	28.42	29.03	21.25
Cyclohexane	12.27	17.18	27.01
Naphthalene	-	0.37	13.02
Methylbenzene	0.51	2.36	11.06
Others	20.49	22.76	2.11

4. Conclusion

Microwave-induced pyrolysis of C6 non-aromatic hydrocarbons produces significant amount of valuable products: gaseous hydrocarbons with light olefins and liquid hydrocarbon oils containing benzene and benzene derivatives. In increasing the temperature was found to enhance the production aromatic compound although the amount of liquid products was lower at higher temperature. Overall, temperature has a significant influence on the overall yields and formation of the recovered pyrolysis gases and liquid oil. It is evident that microwave-induced pyrolysis has a potential to produce valuable products from the low value hydrocarbons.

5. Acknowledgements

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