

# Effective Conversion of Biomass Tar into Fuel Gases in a Microwave Reactor

*by* Samsudin Anis

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# Effective Conversion of Biomass Tar into Fuel Gases in a Microwave Reactor

**Abstract.** This work deals with conversion of naphthalene ( $C_{10}H_8$ ) as a biomass tar model compound by means of thermal and catalytic treatments. A modified microwave oven with a maximum output power of 700 W was used as the experimental reactor. Experiments were performed in a wide temperature range of 450-1200°C at a predetermined residence time of 0.24-0.5 s. Dolomite and Y-zeolite were applied to convert naphthalene catalytically into useful gases. Experimental results on naphthalene conversion showed that conversion efficiency and yield of gases increased significantly with the increase of temperature. More than 90% naphthalene conversion efficiency was achieved by thermal treatment at 1200°C and 0.5 s. Nevertheless, this treatment was unfavorable for fuel gases production. The main product of this treatment was soot. Catalytic treatment provided different results with that of thermal treatment in which fuel gases formation was found to be the important product of naphthalene conversion. At a high temperature of 900°C, dolomite had better conversion activity where almost 40 wt.% of naphthalene could be converted into hydrogen, methane and other hydrocarbon gases.

## INTRODUCTION

Nowadays, research activities on renewable energy sources have become more and more important in order to look for alternatives and greener sources of energy to substitute the fossil fuels. One of the renewable energy sources is biomass that can be processed via thermochemical process of biomass gasification. In this process, biomass is converted into other forms of energy in the presence of an externally supplied gasifying agent such as steam, air or pure oxygen. Biomass gasification is a complex process that generally occurs in the sequence of stages of drying, pyrolysis, oxidation and reduction. During the process, tar is formed primarily as a product through depolymerization from the pyrolysis stage at a relatively low temperature of 200°C to 500°C. In this condition the cellulose, hemicellulose and lignin components of biomass break down into primary tar that contains oxygenates and primary organic condensable molecules. As the temperature increases above 500°C, the primary tar compounds undergo decomposition into smaller molecules, gases and heavier molecules called secondary tar. Further increase of temperature, primary tar products are destroyed and tertiary products are formed. The latter products are mainly composed of Light Poly Aromatic Hydrocarbons (LPAH) such as indene, naphthalene, phenanthrene and anthracene.

Tar presents as the main obstacle in biomass gasification for not only causing serious operational problems in downstream pipeline and end user application but also influence the energy efficiency of the overall process. Tar problem is fundamentally not only concerned with the quantity, but also the composition and properties of the tar that are associated with the tar component and condensation behavior. Concerned with that, LPAH tar have been considered as the main cause of condensation problem as it condenses at relatively low temperature of below 100°C which can block and foul the engine system. Moreover, LPAH tar particularly naphthalene is one of the less reactive tar compounds that is difficult to be eliminated. Therefore, reduction or conversion of tar into valuable products is highly necessary.

A number of tar conversion methods including thermal and catalytic treatments have been developed and reported in numerous literatures. The methods have been found to be effective in reducing tar content by converting the tar into useful gases such as hydrogen, carbon monoxide and hydrocarbon gases. In common, tar conversion is conducted under various parameters including reforming agents, catalysts, reaction temperatures and residence times. Temperature and residence time are considered to be the key factors for radical formation. The presence of catalysts and reforming agents such as steam, hydrogen, oxygen and carbon dioxide can enhance tar conversion at low temperature. Moreover, appropriate implementation of heating strategy by means of microwave irradiation for providing a continuous supply of heat during thermal and/or catalytic conversion of tar offers various advantages such as low energy consumption, reduce process time and improve conversion efficiency.

This work was conducted to reduce tar by means of thermal and catalytic treatments under microwave irradiation. With the aim to convert the tar effectively, dolomite and Y-zeolite were employed and investigated at various temperatures using naphthalene as a biomass tar model compound.

## MATERIALS AND METHODS

## Materials

Naphthalene ( $C_{10}H_8$ ) vapor was used as a tar model compound in this study. It is a light poly aromatic hydrocarbon (LPAH) with single ring compound which is classified as a class 4 tar. To purge the evaporated naphthalene and to keep the atmosphere inert, purified nitrogen (99.999%) was chosen as a carrier gas. Dolomite and Y-zeolite were used to investigate the influence of catalysts on naphthalene cracking. The catalysts were calcined in-situ under air flow for 2 h at 900°C for dolomite and 600°C for Y-zeolite. Dolomite has a particle size of 600  $\mu\text{m}$  with a bulk density of 1.33  $\text{g}/\text{cm}^3$ . It was mainly composed of 34.69 wt.% CaO, 15.06 wt.% MgO and 2.34 wt.%  $\text{SiO}_2$ . Y-zeolite is a commercially powder catalyst (CBV720) with a bulk density of 0.26  $\text{g}/\text{cm}^3$  and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 30. It has a surface area of 780  $\text{m}^2/\text{g}$  and a pore size of 7.4  $\text{\AA}$ . Non catalytic material of silicon carbide (SiC) was also used as an absorber material to increase the reactor temperature. It has a particle size of 2.085 mm and bulk density of 1.48  $\text{g}/\text{cm}^3$ .

## Experimental Apparatus

A schematic diagram of the experimental apparatus is presented in Fig. 1. It consists of three main units: tar model generator, producer gas treatment and product collection systems. Tar model generator system consists of a tar generator and a mixing chamber that were used to evaporate naphthalene and to ensure homogeneity of the evaporated naphthalene and carrier gas mixture, respectively.

Producer gas treatment system includes a modified microwave oven and an alumina reactor containing SiC. The modified microwave oven (Panasonic, NN-SM330M) has a frequency of 2.45 GHz corresponding to wavelength of 12.23 cm. The maximum power consumption and maximum output power of the microwave oven were 1125 W and 700 W, respectively. The alumina reactor with 25.4 mm i.d. and 160 mm length was installed vertically in the microwave chamber and designed as a fixed bed reactor. It contains SiC and a moveable temperature detector (K-type thermocouple) at the center of the reactor. For maintaining the temperature inside the reactor, a temperature controller was also attached to the system. Product collection system consists of tar sampling train, filter papers and gas sampling bags. The tar sampling train has been modified along with the guideline for sampling and analysis of tar and particles in producer gas. The gas passes through a series of six impinger bottles. The first two bottles were placed at atmospheric environment and the second four bottles were immersed in a mixture of ice and salt bath with temperature of about -22°C. In addition, the first five bottles were filled with 50 mL isopropanol whilst the last was empty.

## Thermal and Catalytic Treatment of Naphthalene

For each experiment, naphthalene was evaporated in the tar generator and carried with purified nitrogen gas into the microwave reactor. During the experiment, the purified nitrogen gas was continuously supplied at a particular flow rate to give the desired residence time as well as to maintain inert atmosphere to prevent oxidation of the products. Part of the purified nitrogen flowed through the tar generator and then mixed with the main nitrogen in the mixing chamber to obtain the desired initial concentration of the evaporated naphthalene. A detail of experimental parameters is displayed in Table 1.

For catalytic cracking processes, the catalyst with SiC bed is sandwiched between SiC beds, forming a total bed height of 120 mm within the reactor. In each experimental run, 6 g of dolomite or 3 g of Y-zeolite was mixed with 25 g of SiC. During experiments, before and after leaving the reactor, the gas stream was led into a product collection system to condense the tar as well as to capture the soot/particulate. Once the samples have been collected, isopropanol containing tar in each impinger bottles were mixed together and filtered to separate the particles. The filtered solvent was evaporated by a standard rotary evaporator equipped with solvent library software. Gravimetric tar yield was obtained by the weight of the dry residue normalized by the collected gas volume. The dry clean gas product was collected using gas sampling bags and then analyzed in a Gas Chromatography-Thermal Conductivity Detector (GC-TCD) to quantify the amount of  $\text{H}_2$  and  $\text{C}_1\text{-C}_2$  hydrocarbons using He as a carrier gas. Three samples were taken to obtain the average.

## RESULTS AND DISCUSSION

### Thermal Treatment

Thermal treatment processes were conducted at various temperatures to examine the degree of naphthalene conversion. The influence of increasing temperature on the enhancement of naphthalene conversion can be clearly observed in Fig. 2. In this case, naphthalene conversion was studied at a constant residence time of 0.5 s and temperatures ranging from 900°C to 1200°C. As indicated in the figure, naphthalene conversion seemed fairly thermally stable at temperatures of below 1100°C. The result showed that only around 24% of naphthalene conversion efficiency was achieved at a temperature of 1050°C. Naphthalene conversion increased significantly with the increase of temperatures from 1100-1200°C. At these conditions, although the formation of gaseous products increased



considerably particularly hydrogen, soot appeared as the major product from thermal treatment of naphthalene. Under experimental conditions, the highest conversion efficiency of about 91% was obtained at the highest temperature tested of 1200°C. This cracking reaction temperature substantively is much higher compared with the necessary cracking temperature of other tar model compounds such as phenol (750°C) and toluene (1050°C). It means that naphthalene is having little tendency to be cracked thermally.

Figure 3 shows the yields of gas products from thermal treatment of naphthalene. As a consequence of the improvement of conversion efficiency described above, in general all the produced gas species also increased significantly as temperature increases. It can be seen that in the range of temperatures investigated, generally H<sub>2</sub> was markedly found to be the main gas products. Moreover, at temperatures of below 1050°C only H<sub>2</sub> and a little bit of CH<sub>4</sub> gases were observed. The more drastic improvement in the yields of H<sub>2</sub> and CH<sub>4</sub> at higher temperatures is partially attributed to the high activity of tar (C<sub>x</sub>H<sub>y</sub>) cracking reactions as given in Equations (1-4). At the highest temperature tested of 1200°C, the high yield of total gases of 19 wt.% was attained in which more than 60 wt.% of total gases was composed of H<sub>2</sub>.

## Catalytic Treatment

### *Effect of Catalyst*

Effect of catalysts on naphthalene conversion was examined at a temperature of 700°C using dolomite and Y-zeolite catalysts. The results as figured out in Fig. 4 found that Y-zeolite showed higher tar cracking activities in comparison with dolomite. Naphthalene conversion efficiencies of about 33% and 79% were observed for dolomite and Y-zeolite, respectively. The differences of physical and chemical properties of both catalysts as previously described are attributed as the main reason of the difference in their activity.

Physically the average pore diameter of dolomite is commonly above 7 nm whilst Y-zeolite has a pore size of about 0.74 nm. On the other hand, molecular dimension of naphthalene is below 0.73 nm. This indicated that the pore sizes of both catalysts allow naphthalene to diffuse into their pores during cracking process. In most cases, the higher catalytic activity of Y-zeolite compared to dolomite is, however, due to its acidic nature that supports cracking reaction of naphthalene. Moreover, the high activity of Y-zeolite is also due to it has higher surface area (780 m<sup>2</sup>/g) than dolomite.

### *Dolomite Catalytic Treatment*

Effect of temperature for catalytic treatment of naphthalene using dolomite as a catalyst is shown in Fig. 5. In this case, the catalytic treatment process was conducted in the temperatures range of 700-900°C. These temperatures were applied in order to minimize the effect of thermal cracking as already been presented previously. As shown, the activity of dolomite for catalytic conversion of naphthalene depends highly on temperature reaction.

It can be observed from Fig. 5 that almost 2 folds of naphthalene were reduced from 700°C to 850°C. In this condition, naphthalene was mainly converted into smaller tar molecules and solid carbonaceous material or coke trapped upon dolomite surface. A small portion of dolomite turned black particularly at the bottom part and the remainder turned grey. This is due to dolomite having higher pore size allows reaction of naphthalene on the surface and in the interior of dolomite. If a tar molecule is adsorbed on the entrance of macro-pore, it then cracked to produce smaller tar molecules, light gases and coke. The smaller tar molecules can further be diffused into meso-pores where it can again be adsorbed and cracked. In contrast, naphthalene did not removed significantly at high temperatures studied particularly from 850°C to 900°C. This is due to at high temperatures, conversion rate of the cracked products such as smaller tar molecules and coke into gases is higher than that of the parent material of naphthalene as indicated in Fig. 6.

The yield of useful gases from naphthalene after cracked by dolomite can be observed in Fig. 6. In the range of temperatures investigated, this method tends to produce H<sub>2</sub> as an important gas product that is similar to gas compositions formed via thermal treatment process as earlier presented. Its production increased considerably with the increase of reaction temperature. It can be concluded that the exponential improvement of H<sub>2</sub> yield as temperature increases could be attributed to secondary reactions of the high conversion activity of the cracked products. The result demonstrated that the highest yield of total gases of 38 wt.% was obtained at 900°C. From this value, almost 70 wt.% of total gases was composed of H<sub>2</sub>.

### *Y-Zeolite Catalytic Treatment*

Y-zeolite as a catalyst was applied to reduce naphthalene at various temperatures. Experiments were performed in the relatively lower temperature range of 450-700°C in order to avoid thermal degradation of Y-zeolite. The results shown in Fig. 7 indicated that naphthalene conversion efficiency increased significantly as the temperature increases up to 650°C. The increase in removal efficiency with increase in temperature during naphthalene removal suggests the increasing role of cracking reaction and coke formation. The large surface area, pore size and acidic nature of Y-zeolite also support cracking reaction and coke formation. At these conditions naphthalene was primarily converted into coke and also benzene rather than useful gases. Further increase in temperature, Y-zeolite does not

convert naphthalene significantly. This behavior is mainly affected by coke formed inside Y-zeolite pores and then deactivates catalyst activity by pore blockage thus lowering the surface area. Nevertheless, under experimental conditions, the highest conversion efficiency of naphthalene was achieved at 700°C. In this condition 79% of naphthalene was successfully converted into other products.

Figure 8 shows the yields of gas products from catalytic treatment of naphthalene using Y-zeolite. As shown, very few of gases were obtained from naphthalene conversion using Y-zeolite. At temperatures of 450-600°C, below 4 wt.% of each gas was produced in which C<sub>2</sub> hydrocarbons were the major component of gases. Above 600°C, CH<sub>4</sub> was markedly appeared as the main gas products. The more drastic improvement in the yields of CH<sub>4</sub> and also H<sub>2</sub> at higher reaction temperatures suggests the increasing role of cracking reactions. Another reason regarding this behavior is the high volatility of coke precursors with increasing reaction temperature and their conversion into gas species. As a result, at a temperature of 700qC, the yield of total gases increased significantly of about 22 wt.% where about 60 wt.% of this value was occupied by CH<sub>4</sub>.

## CONCLUSIONS

Conversion of naphthalene as a biomass tar model compound through thermal and catalytic treatments in a microwave reactor has been investigated. Similar tendency of naphthalene conversion efficiency was obtained in both treatments where naphthalene could be reduced effectively at high temperatures. Although the high reaction temperature of thermal treatment provided the highest naphthalene conversion, it was not appropriate for useful gases production. Similar result was obtained via Y-zeolite catalytic treatment. CH<sub>4</sub> appeared as the main useful gas products during thermal and catalytic treatment using Y-zeolite. On the other hand, although dolomite had lower conversion efficiency compared to Y-zeolite, it was found to be a better approach for conversion of naphthalene into fuel gases. This approach was able to produce almost 40 wt.% gases at a temperature of 900qC where H<sub>2</sub> was the major gas components.

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