THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Chemical Engineering)
DEGREE

Chemical Engineering	Chemical Engineering
FIELD	**DEPARTMENT**

TITLE: Catalytic Upgrading of Bio-oil from Pyrolysis of Soybean Cake using HZSM-5/MCM-41 Catalysts

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THESIS

CATALYTIC UPGRADING OF BIO-OIL FROM PYROLYSIS OF SOYBEAN CAKE USING HZSM-5/MCM-41 CATALYSTS

NITI NINCHAWEE

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Chemical Engineering)
Graduate School, Kasetsart University
2009

Niti Ninchawee 2009: Catalytic Upgrading of Bio-oil from Pyrolysis of Soybean Cake using HZSM-5/MCM-41 Catalysts. Master of Engineering (Chemical Engineering), Major Field: Chemical Engineering, Department of Chemical Engineering. Thesis Advisor: Associate Professor Apinya Duangchan, Ph.D. 72 pages.

Bio-oil from soybean cake was produced by pyrolysis in a fixed bed reactor and characterized in terms of high heating value and chemical class composition. Soybean cake collected from waste of soybean milk production was dried and ground until its diameter was 0.250-0.850 mm. Pyrolysis reaction took place under nitrogen atmosphere with a heating rate of 2 K min^{-1} in a semi-batch reactor from room temperature to 673 K and 250 g of biomass was used in each reaction. The yield of bio-oil was 48%wt of biomass and the high heating value (no water) of organic phase of the bio-oil was 19.9 MJ/kg of the organic phase. Bio-oil contained 29%wt of aliphatic fraction and 21%wt of asphaltene.

MCM-41 and HZSM-5 catalysts were used to upgrade bio-oil properties and mixtures of MCM-41 and HZSM-5 at ratios of 1:1, 1:2 and 2:1 were investigated their activities. Upgraded bio-oil by MCM-41, the bio-oil showed the highest high heating value of 38.5 MJ/kg of the organic phase of bio-oil at 673K. Moreover, aliphatic compounds increased from 29 to 47%wt and asphaltene compound decreased from 21%wt to 16%wt. The effect of sequence of catalysts packing was investigated by using of two conditions; order packing and random packing. MCM-41 and ZSM-5 with the ratio of 1:1 showed the best performance among other ratios. In addition order packing showed the best performance by increasing high heating value to 38.5 MJ/kg of the organic phase of bio-oil. The optimum upgrading temperature is 673K. Spent MCM-41 and HZSM-5 were regenerated by heat at 773 K in the presence of air for 12 h to remove the coke deposited. MCM-41 which was used and regenerated two times showed no significant change in its activity.

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ACKNOWLEDGEMENTS

First, I would like to give my sincere thank and express my respect to my advisor, Associate Professor Apinya Duangchan, for giving the valuable knowledge and suggestion. I would like to thank my co-thesis advisor, Assistant Professor Attasak Jaree for giving comments and approving my thesis. I also thank staff of the Department of Chemical Engineering, Kasetsart University for their support on my work. I would like to thank my family and friends for giving moral support for my study.

For financial support, I would like to thank Kasetsart Unversity Research and Development Institute (KURDI) and National Center of Excellence for Petroleum, Petrochemical and Advanced Materials (PPAM).

Niti Ninchawee
September 2009

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INTRODUCTION

At present, energy crisis is a main problem worldwide. Biomass offers a great potential for solving energy crisis in Thailand because of a lot of wastes from agriculture. Biomass can be directly used as a fuel source for combustion, however, utilization of biomass was limited due to the different forms of biomass. Some researchers tried to convert biomasses into bio-oil by pyrolysis reaction. Wang *et al.* (2006) produced bio-oil from biomass by pyrolysis rice straw in a closed reactor at 553-773 K. The maximum yield of oil was 10 wt% while Qian *et al.* (2005) produced bio-oil from silver birch wood and water in an autoclave reactor at 553-693 K. The maximum yield of oil was 53.3 wt% and Uzun *et al.* (2005) pyrolysed soybean cake at 673-973 K in a fixed-bed reactor with 38.7 wt% of maximum oil yield. Bio-oils are easier to handle and have higher heating values than their raw materials.

However, the heating value of bio-oil is not good enough to replace petroleum fuel. Using of cracking catalyst was aimed at improving bio-oil properties. MCM-41 is a member of a family of mesoporous materials which has a narrow pore size distribution. Adam *et al.* (2006) upgraded bio-oil of spruce wood by MCM-41 and found an increase of hydrocarbon and phenol but a reduction of acid contained in bio-oil. MCM-41 is an interesting catalyst for its ease of preparation and lower price than HZSM-5. Moreover, soybean milk is produced daily and soybean cake is a good source for bio-oil. Upgrading of bio-oil from spruce wood by MCM-41, Cu- MCM-41 and Al- MCM-41 were reported by Adam *et al.* (2006), however, bio-oil from different biomasses (Miscanthus and Spruce wood) gave opposite results. Upgrading of bio-oil from soybean cake by MCM-41 was not reported.

HZSM-5 is a microporous material which can selectively conduct cracking and isomerization of long chain hydrocarbon into a mixture of light aliphatic (C1-C6) and aromatic (C6-C10) hydrocarbons (Wang, 2006). HZSM-5 can easily be deactivated by coke deposition. Vitolo *et al.* (2001) upgraded pyrolytic oils by HZSM-5 and prolonged upgrading cycle by heating HZSM-5 at 500°C in the presence of air to remove coke deposit in catalyst.

In this study, HZSM-5 and MCM-41 were used as catalysts to upgrade bio-oil from soybean cake. Effect of the mixture of MCM-41 and HZSM-5 on the catalyst activity was investigated. Mixed mesoporous catalyst with microporous catalyst may have synergistic effect on bio-oil property and coke deposit.

Regeneration of catalyst by heating in the presence of air to remove coke deposite in the catalyst was investigated. Bio-oil was analyzed in terms of chemical class composition followed the procedure of Uzun *et al*. (2006), which the amounts of aliphatic, aromatic, polar and asphaltene in bio-oil were identified, and of heating value which was not reported by Uzun *et al.* (2006).

OBJECTIVES

1. Upgrading of bio-oil from soybean cake by using MCM-41, HZSM-5 and mesoporous material from zeolite (MMZ) catalysts

2. Study the synergistic effect of HZSM-5 and MCM-41

Working scope

Bio-oil was produced from soybean cake by pyrolysis in a fixed bed reactor. Pyrolysis reaction took place under nitrogen atmosphere with a heating rate less than 10 K/ min (slow pyrolysis) from room temperature to 573- 673 K. Soybean cake diameter was less than 1.00 mm. Bio-oils were upgraded by HZSM-5: MCM-41 with ratios of 1:2, 1:1 and 2:1. Spent catalysts were regenerated by heating in the presence of air for 12 h. Bio-oil was characterized in terms of high heating value and chemical class composition.

Impact of result

This research studies the new way to improve bio-oil from pyrolysis of soybean cake. Bio-oil quality is better after upgraded by HZSM-5 and MCM-41. Value is added to soybean cake.

LITERATURE REVIEW

Biomass

Biomass refers to living and recently dead biological material. It can be used as a source of energy like petroleum oil or coal but its advantage is renewable energy. Biomass can be directly used as fuel for heat and electricity generation and raw material for liquid fuel producing. Biomass is an organic material from both plant and animal such as hazel nut, lemon peel, cattle manure, molasses and soybean cake. It contains long chain hydrocarbon which consists of carbon, hydrogen, oxygen and nitrogen but different biomasses contain different ratios of element which affect physical properties. The ratio of hydrogen to carbon (H/C) and the ratio of oxygen to carbon (O/C) affect heating value and stability of the bio-oil and they were used to determine petroleum oil property.

Biomass properties are different from petroleum oils for it has much less carbon and more oxygen and has a lower heating value than petroleum oil. It can be seen from Figure 1 (Wang, 2007) that the H/C molar ratio in the petroleum is in the range of 1.5–2.0, and the O/C molar ratio is lower than 0.06, while in wood, the H/C is less than 1.5 and O/C molar ratio is over 0.3. Thus, in order to realize the conversion of biomass to the liquid products that can substitute petroleum, the ratio of H/C must be in the range of petroleum oil and while the ratio of O/C decrease. For the liquid products, the yields of oxygenous compounds should be decreased to the minimum, however, the liquid products properties depend on biomass properties (Miskolczi, 2009).

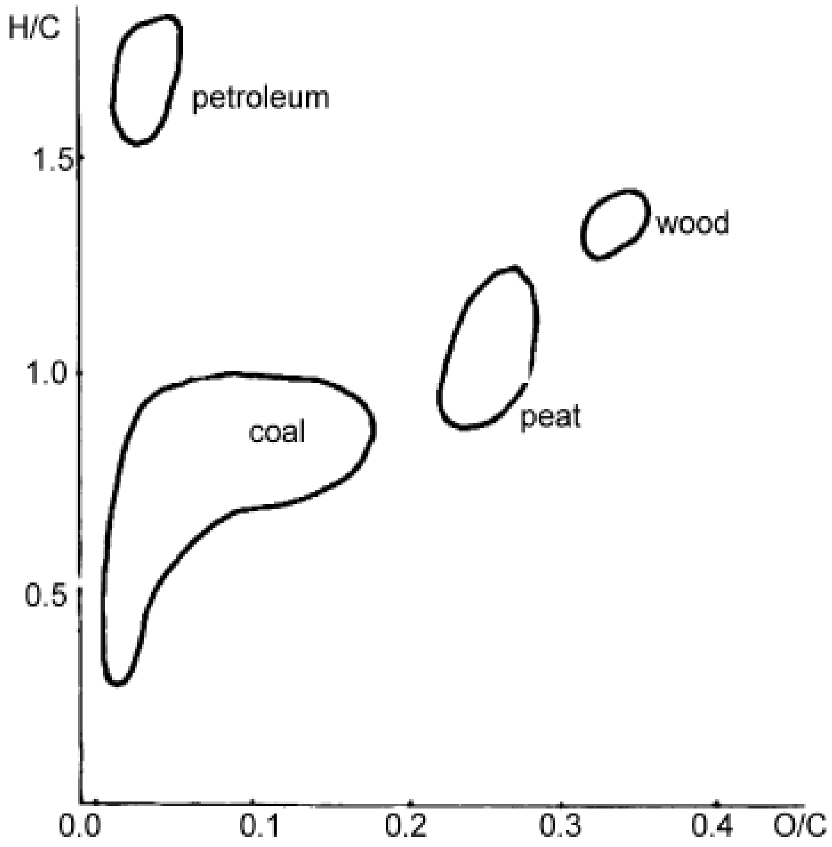

Figure 1 The elemental content of coal, petroleum and wood

Source: Wang (2007)

Soybean

Soybean or glycine max is grown a lot in East Asia. The chemical composition are oil and protein content together account for about 50% of dry soybean by weight, protein of 48% and oil of 2% (Uzun 2006). Soybean contains a lot of protein so it is a good use as food. It was used as ingredient in a lot of Asian menu, for example tofu, soybean milk and soybean oil. Therefore, a lot of soybean cake was produced during soybean milk and soybean cake production. The main characteristics of soybean cake are shown in Table1.

Table 1 Main characteristics of soybean cake

Characteristics	Soybean cake
Moisture content (%)	8.38
Oil content (%)	2.18
Holocellulose content (%)	5.00
Protein content (%)	44.37
Proximate analysis (%)	
Volatiles	71.60
Fixed carbon	14.39
Ash	5.63
Ultimate analysis (%)	
Carbon	55.89
Hydrogen	6.57
Nitrogen	9.29
Oxygen	28.25
Empirical formula	$CH_{1.4}N_{0.14}O_{0}$
H/C molar ratio	1.41
O/C molar ratio	0.38
Higher calorific value (MJ/kg)	23.23
Bulk density (kg/m^3)	680

Source: Uzun (2006)

Soybean can be thermally cracked to produce bio-oil.

Thermal cracking

Thermal cracking or thermolysis is to use high temperature to break bond in long chain hydrocarbon. The main form of feedstock by thermolysis is shown in Figure 2. When decomposition without air, it is called pyrolysis. When it is performed in hydrogen atmosphere, it is referred to hydrogenation. If it is carried out in the presence of a controlled amount of oxygen, then it is known as gasification.

Depending on the conversion route employed, the end products vary in composition and quality.

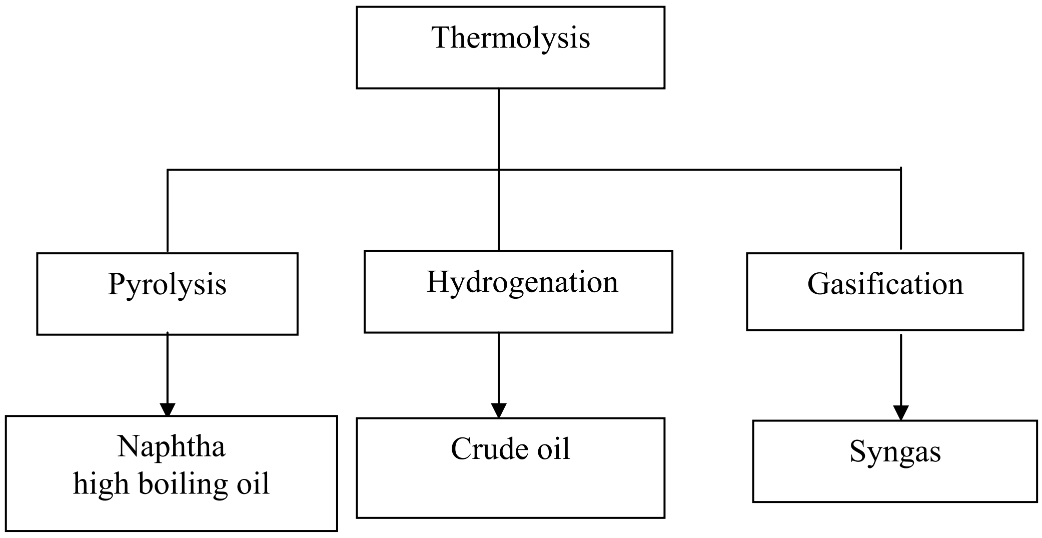

Figure 2 Overview of the main form of biomass feedstock by thermolysis.

Source: Huber (2006)

Pyrolysis is carried out in a reducing atmosphere (i.e. in the absence of air) at temperature of up to 1073K. During pyrolysis reaction, biomass can be converted into petrochemical feedstocks such as naphtha, liquid and wax-like hydrocarbons and gases. Some researchers have studied pyrolysis reaction for various kinds of biomass.

Wang *et al.* (2007) produced bio-petroleum from biomass by pyrolysis rice straw in a closed system reactor at 553-773 K. The heating rate was 10 K/min. The maximum yield of oil was 10 wt% at 693 K. The oil product has mole ratio of H/C equal to 1.65 and mole ratio of O/C equal to 0.058 which is in the range of petroleum oil. The results from H^1NMR and FT-IR showed that oil product contained alkane compounds and aromatic compounds.

Qian *et al.* (2005) produced bio-oil from silver birch wood and water in an autoclave reactor at 280-420°C, 8 MPa and used sodium carbonate as a catalyst in the

H_2 atmosphere. The maximum yield of oil was 53.3 wt% at 380°C. The product was heavy oil containing hydrocarbon, aldehyde, ketone, hydroxybenzene and ester.

Uzun *et al*. (2005) pyrolysed soybean cake at 400-700°C in a fixed-bed reactor. Some effects such as temperature, N_2 flow rate, heating rate and particle size on product yield were investigated. The maximum yield of oil was 38.72 wt% at 550°C, 39.50 wt% with a particle size range of $0.425 < Dp < 0.85$ mm, 41.42 wt% at a sweeping gas flow rate of 200 cm^3 min^{-1} and 42.83 wt% at a heating rate of 700 °C min^{-1}. The oil products were quite similar to currently utilized transport fuels.

Mechanism of thermal cracking

Thermal cracking is cracking of long chain hydrocarbon by using of high temperature therefore radical pathways were occurring during thermal cracking. When multiple paths are available for a given type of bond-breaking reaction, the path that involves cleavage of the weakest chemical bond is expected to be the fastest path. These reaction families are displayed in Figure 3. They include homolytic dissociation and its reverse, radical recombination; radical disproportionation and its reverse, molecular disproportionation; b-scission and its reverse, radical addition to an unsaturated carbon; isomerization and hydrogen abstraction (Savage, 2000).

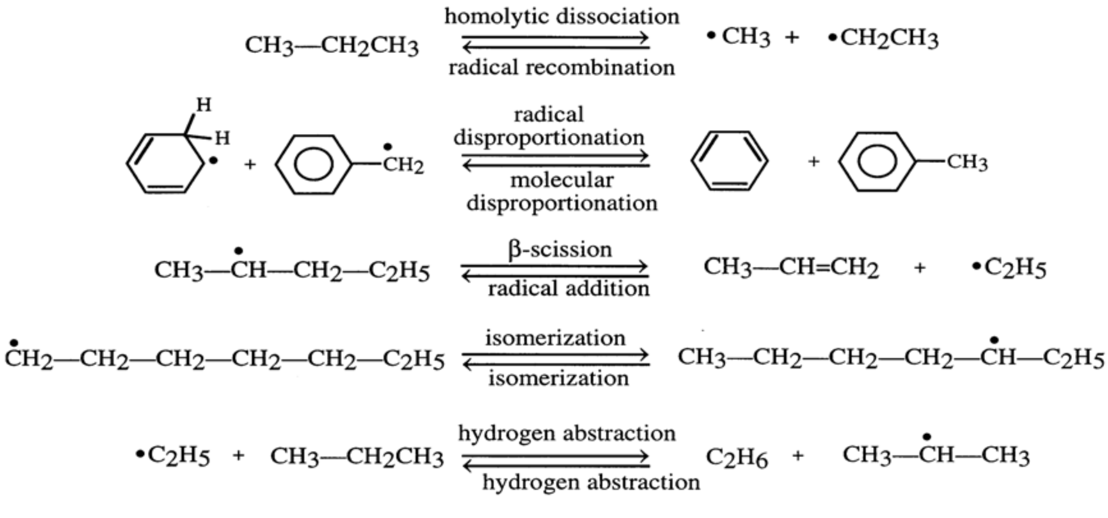

Figure 3 Main reaction families for hydrocarbon pyrolysis.

Source: Savage (2000)

Zeolite Catalyst

The produced bio-oils, however, are not stable and contain high oxygen content. Upgrading is, therefore, necessary using catalysts such as HZSM-5 and MCM-41.

Zeolite was found by Cronstedt in 1756. The structure of zeolite is the connection between the tetragonal of $[SiO_4]_{4-}$ and $[AlO_4]_{5-}$. Oxygen atom is the connection point in the structure. The structure separates into 8 sub-units (repeating unit in the structure) which are called secondary building units (SBUs) as shown in Figure 4.

In the case of acidic zeolite-type catalyst, it is suggested that the heavy organics are cracked into light organics and it deposits on the catalyst surface where it may act as coke precursors. The light (mainly oxygenated) organics are cracked, deoxygenated (dehydration is the main route), decarboxylated and decarbonylated. Through a carbonium ion mechanism, oligomerisation of the cracked fragments, followed by alkylation, isomerisation, cyclisation and aromatisation produce a mixture of light aliphatic (C1-C6) and aromatic (C6-C10) hydrocarbons. Some of the aromatic hydrocarbons polymerize to form coke (Wang *et al*., 2006).

The structure of zeolite is very uniform, it has narrow pore size distribution and high pore volume. Its narrow pore size distribution makes it appropriate to be used as molecular sieve and its high pore volume makes it appropriate to be used as adsorber. The ability to exchange ion makes zeolite appropriated to be used as a catalyst for hydrocracking, catalyst cracking, reforming, C_5/C_6 isomerization and benzene alkylation. This experiment is interested in using HZSM-5 which is one of the zeolite family to convert long chain hydrocarbon into a mixture C_1-C_6 straight and aromatic hydrocarbons which is more valuable.

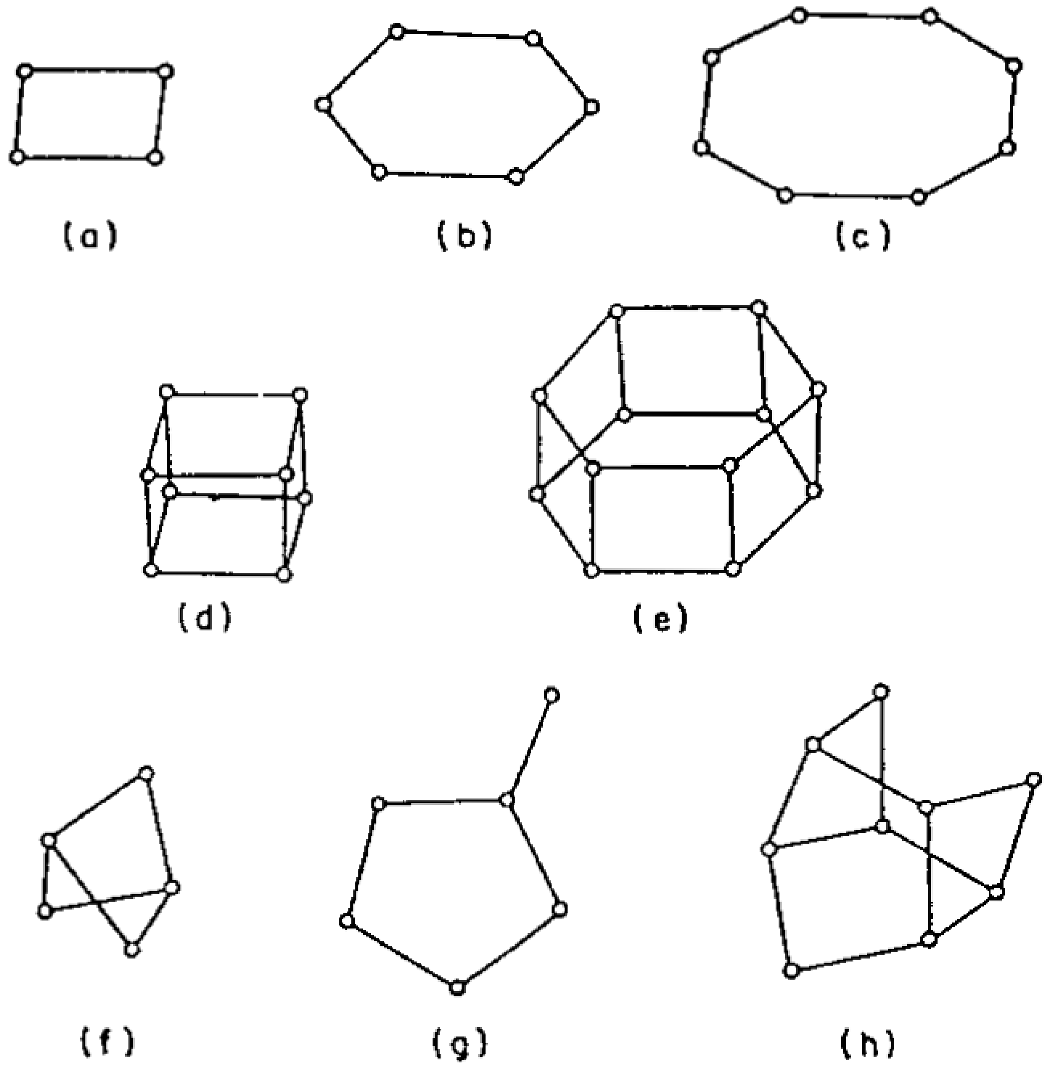

Figure 4 Secondary building Units (SBUs) of zeolite structure (a) single four rings (S4R), (b) single six rings (S6R), (c) single eight rings (S8R) (d) double four rings (D4R) (e) double six rings (D6R) (f) complex 4-1 (g) complex 5-1 (h) complex 4-1-1

Source: Karakoulia *et al.* (2008)

HZSM-5 Catalyst

HZSM-5 was first synthesized in 1972 by Mobil. It is pentasil in zeolite family. Its secondary building units are complex 5-1 which has five oxygens in unit ring (five-membered ring) as shown in Figure 5.

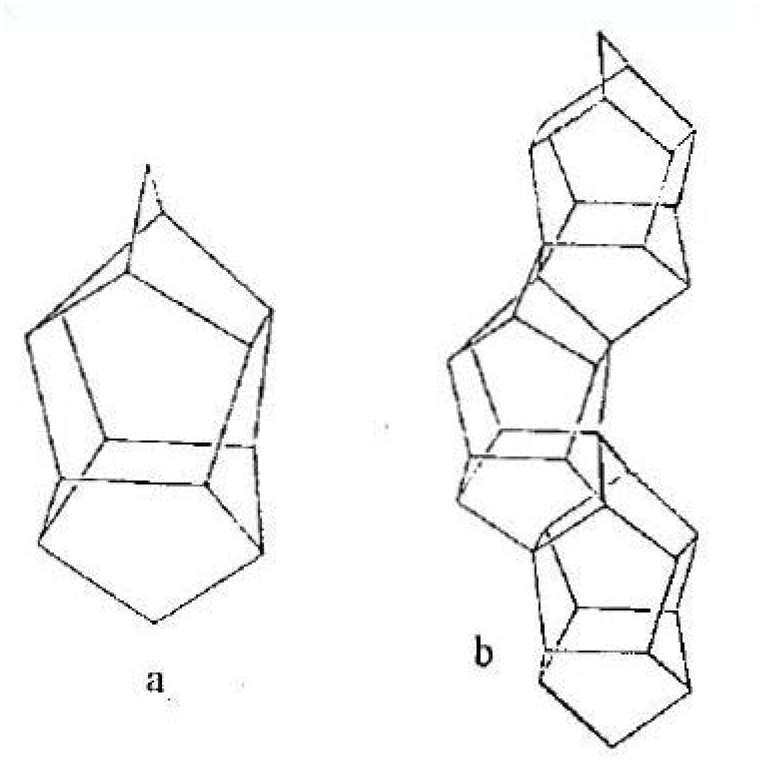

Figure 5 HZSM-5 building unit (a) Secondary Building Units (SBUs) of HZSM-5 (b) Connection of Secondary Building Units (SBUs) of HZSM-5

Source: Karakoulia *et al.* (2008)

Ten secondary building units connected together to form microporous material as shown in Figure 6. HZSM-5 has two types of pore in material. First type is straight channel which is open oval shape hole; cross section area is equal to 0.51 x 0.55 nm^2. The other type is sinusoidal channel which is circle shape hole, cross section area is equal to 0.54 x 0.56 nm^2 and has zigzag channel. Zeolite crystal is usually orthorhombic form but sometime can be monoclinic form.

HZSM-5 has cation in its structure which is active to double bond in hydrocarbon molecule so HZSM-5 is appropriated to be used as a cracking catalyst. Otherwise, it can be used as a catalyst in alkylation, dewaxing, isomerization of light paraffin and reforming of naphtha. The study about the behaviour of HZSM-5 zeolite on upgrading of pyrolytic oils has been reported (Miskolczi *et al*, 2009).

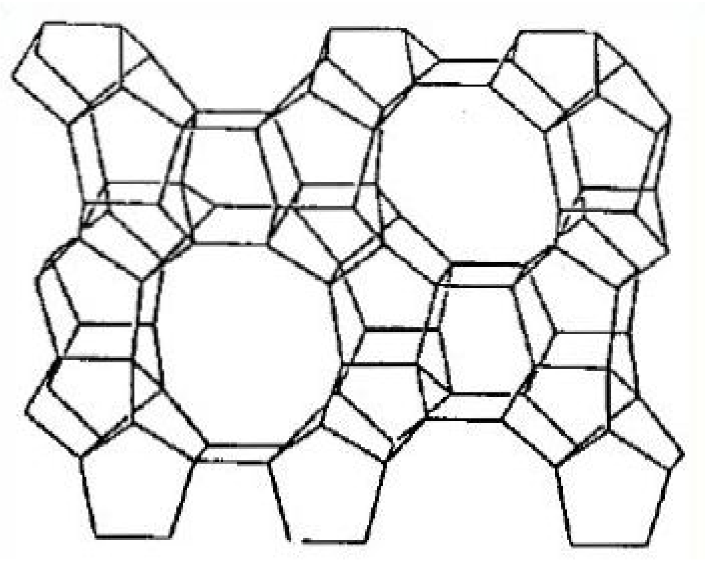

Figure 6 Structure of HZSM-5

Source : Karakoulia (2008)

Miskolczi *et al.* (2009) pyrolyzed waste of plastic (HDPE and PP) in pilot scale. Waste plastics were decomposed in a tube reactor at 793K, using hourly feed rate of 9.0 kg. For supporting the more intensive cracking of C\C bonds of main polymer structure a commercial HZSM-5 catalyst was tested in concentration of 5.0%. Products were separated into gases, gasoline, light and heavy oil by distillation. Plastic wastes could be converted into gasoline and light oil with yields of 20–48% and 17–36%, respectively. The gas and liquid products had significant content of unsaturated hydrocarbons, principally olefins. In the presence of HZSM-5 catalyst the yields of lighter fractions (especially gasoline) could be considerably increased and the average molecular weight of each fraction has decreased.

Vitilo *et al.* (2001) investigated upgrading of pyrolytic oils over HZSM-5 zeolite. The behaviour of HZSM-5 zeolite was studied in repeated upgrading-regenerating cycles. HZSM-5 was appropriated to be used in deoxygenation, decarboxylation, decarbonylation, cracking, oligomerization, alkylation, isomerization, cyclisation and aromatization. After regeneration at 773K repeatedly, zeolite lost activity. The loss of activity is mainly connected to the disappearance of a significant amount of acidic sites.

Aho *et al.* (2008) investigated the influence of zeolite structure on catalytic pyrolysis of pin woody in a fluidized bed reactor with three coolers. The reaction temperature in the experiment was 723 K. The heating rate was 10 K/min and feed rate was close to 20 g/h. Four types of zeolite were used, HZSM-5, Mordenite-zeolite, Beta- zeolite and Y- zeolite to upgrade bio-oil. The efficiency of upgrading were indicated in terms of yield (wt%) of different product phases (oil, water, char, coke and gas) from different bed materials (quartz sand, HZSM-5, Mordenite- zeolite, Beta- zeolite and Y- zeolite) and in terms of groups of chemicals in bio-oil (acids, alcohols, ketones, aldehydes, phenols and polyaromatic hydrocarbons (PAHs). The results showed that HZSM-5 gave the highest amount of oil yield and bio-oil from upgrading of HZSM-5 also contained the lowest acid and the highest ketones group. Spent catalysts were regenerated by heating in an oven at 450 K for 2 h. The initial structures after regeneration of zeolite was not affected.

MCM-41 Catalyst

MCM-41 is one member of a family of mesoporous materials, first synthesized in 1992 by Beck *et al.* (1992). MCM-41 possesses a nearly monodisperse array of straight, unconnected pore channels with diameters that can be tailored in the range 1.6-10 nm. The pores are thought to be roughly cylindrical in shape, although some researchers suggest a hexagonal cross section. Transmission electron microscopy (TEM) shows the pores to be arranged in a regular hexagonal array. This hexagonal arrangement is thought to lose some regularity for interpore distance (the lattice parameter) of more than 4 nm, and the very narrow pore size distribution characteristic of the material also becomes broader as the lattice parameter increases.

The synthetic approach used to produce MCM-41 involves templating of surfactant liquid crystal structures and can also be manipulated to yield cubic or lamellar phases. The solid skeletal structure of MCM-41 has been synthesized as pure silicated, aluminosilicate, or titanosilicate. No clear evidence for highly crystalline walls has been found, and the broad range of Si-O-Si bond angles seen in solid state. NMR studies suggest an amorphous or partially crystalline structure, more closely related to amorphous silica. NMR also suggests that 20% (±10%) of the silicons in MCM-41 are present as silanol species. At its thinnest point between pores, the wall thickness has been estimated to be in the range 0.8-3.0 nm from experiment, and a theoretical model suggests a figure from 0.8 to 1.3 nm, based on the comparison of simulated X-ray diffraction data for the model with experimentally determined diffraction results. The density of the SiO_2 material in the theoretical model, measured as the T-site density per nm, is between 6.8 and 11.6, based on the reported average Si-Si separation in an earlier bulk silica model, and the T-site density of zeolites (11-18T-sites per nm). These densities include the pore spaces as well as the wall structure (Maddox, 1997).

MCM-41 is of particular interest because it fills two important roles,

1) Its narrow pore size distribution and straight, unconnected channels make it an ideal model adsorbent for fundamental theoretical studies of fluid behavior in confined regions.

2) Its large and controllable pore size enables it to host much larger molecules than alternative catalytic materials.

There are some studies on the effect of MCM-41 on bio-oil yield.

Iliopoulou *et al.* (2007) investigated the effect of acidity and porosity of MCM-41 and Al-MCM-41 on percent weight of desired product (bio-oil). MCM-41 and Al-MCM-41 were used at different ratios of Si/Al. Different ratios of Si/Al make

Jun-ming *et al.* (2008) upgraded bio-oil by using Zr-MCM-41 as a solid acid catalyst. The operation conditions for bio-oil upgrading were as follows: catalyst usage based on bio-oil = 4%wt; reflux ratio = 1: 6; mass feed ratio of bio-oil: ethanol: hydrogen peroxide (aqueous solution 30%) = 1: 0.5: 0.4. Under these conditions, two kinds of upgraded bio-oils (light oil and heavy oil) were obtained. Their density was reduced from original 1.16 kg/m^3 to 0.91 kg/m^3 and 0.95 kg/m^3, water content from

33% to 0.52% and 5.03%, whereas, the gross calorific value increased from original 14.3 MJ/kg to 21.5 MJ/kg and 24.5 MJ/kg, and the pH value from 2.82 to 7.06 and 5.35, respectively.

MATERIALS AND METHODS

Materials

Soybean cake obtained from waste of soybean milk production was dried at 373 K for 24 hours, cut into small particles by blender, and then sieved. Particle diameter between 0.250-0.850 mm was used in the experiment.

1. Preparation of catalysts

Three types of catalyst are used in this study: MCM-41, HZSM-5 and mesoporous materials from zeolites (MMZ).

1.1. MCM-41

The as-synthesized mesoporous silica host (MCM-41) was prepared by a surfactant assembly pathway based on charge matching between surfactant and inorganic silica precursors.

The molar ratio of reactant was 0.147 CTAB : 1 SiO_2 : 2.16 NaOH : 148.94 H_2O. Cetyltrimethylammonium bromide (CTAB) was dissolved in deionized water until clear solution was obtained before an addition of sodium hydroxide and sodium silicate (27%) to form precipitation. The pH of the solution was adjusted to 10.7 by 1 molar of hydrochloric acid. The mixture was vigorously stirred for 48 hours using a magnetic stirrer. Finally, the precipitate was filtered, washed and dried at 373 K for 1 hour, then calcined at 813 K for 6 hours (Grisdanurak, 1997). The obtained catalyst was characterized by X-ray diffraction (XRD).

1.2. HZSM-5

The HZSM-5 (Si-Al = 22-25) zeolite sample was supplied by SÜD-CHEMIE AG in the form of Na-HZSM-5. The zeolite material (Na-form) was converted to H-form by refluxing the sample at 353 K, in the presence of aqueous solution of NH_4OH with liquid/solid ratio of 20, and continuously stirred for 72 h. The zeolite was calcined in a furnace for 6 h at 873 K to obtain HZSM-5. The zeolite

HZSM-5 had surface area of 150 m^2 g^{-1}, pore diameter of 0.55 nm, and acidity of 0.52 mmol g^{-1}.

1.3. Mesoporous materials from zeolites (MMZ)

Mesoporous material from zeolite (MMZ) was synthesized followed Hyung *et al.* (2008) procedure. HZSM-5 was dissolved in a NaOH solution which was prepared by dissolving 1.5 g of NaOH in 5.0 g of deionized water. 2.25 g of HZSM-5 was as added to the NaOH solution under magnetic stirring, producing a clear solution. The dissolved zeolite solution was diluted by 2.5 g of deionized water. Then 4.6 g of cetyltrimethylammonium bromide (CTAB) was dissolved in 70 g of water. The zeolite solution was added drop wise into the CTAB solution under vigorous stirring, and was stirred further for 24 h at room temperature. Subsequently, the reaction mixture was heated at 373 K for 24 h. The white precipitate was filtered, washed with water, and dried at 373 K overnight. The MMZ material obtained was washed with an 1 molar of HCl and finally calcined at 823 K for 3 h to remove the surfactant.

2. Catalyst characterization.

MCM-41

The MCM-41 (prepared) was characterized by X-ray diffraction (XRD). The appropriate 2θ is 1-7 (low angle) which should have peak at 2θ = 1.00, 1.10 and 2.00. The physical properties such as porosity, pore distribution and pore size were characterized by autosorb.

H-ZSM-5

The H-ZSM-5 catalyst was characterized by autosorb

MMZ

The MMZ was used as prepared.

Methods

1. Pyrolysis of soybean cake

The pyrolysis experiments were carried out in nitrogen atmosphere. In this study, 316 stainless steel pyrolysis reactor (700 ml) was heated by a furnace with autotuning PID temperature controller using a K-type thermocouple placed in the furnace as shown in Figure 7. The desired flow rate of the carrier gas (N_2) was adjusted and maintained by using a needle valve.

First of all, 250 g of soybean cake was placed in the pyrolysis reactor and then heated by electric resistance from room temperature to 673 K (heating rate 2 K/min). The temperature was measured using calibrated thermocouples. When temperature inside the reactor reached 673 K it was maintained at this temperature for 1 hour. The vapor entered the tube reactor where catalyst about 0.1 %wt of biomass was held on a plug of quartz wool The liquid products passed thru a condenser (285 K) and collected in a flask sitting in an ice plus salt bath. Gas products were sent into gas hood. The temperature of the tube reactor was varied from 623-723 K in order to study the effect of temperature on upgrading process

2. Upgrading of bio-oil.

Bio-oil was upgraded using the same equipment as pyrolysis experiment but the tube reactor (number 6 in Figure 6) was packed with catalysts: MCM-41: HZSM-5 with various ratios (1:2, 1:1, 2:1), MCM-41, HZSM-5 and MMZ. Effect of temperature 623- 723K and sequence of catalysts packing were also investigated.

3. Catalyst regeneration

Catalysts can be deactivated by coke deposited. In order to remove the coke, spent catalysts were regenerated followed the procedure of Vitolo (2001) by heat at 773 K in the presence of air for 12 h.

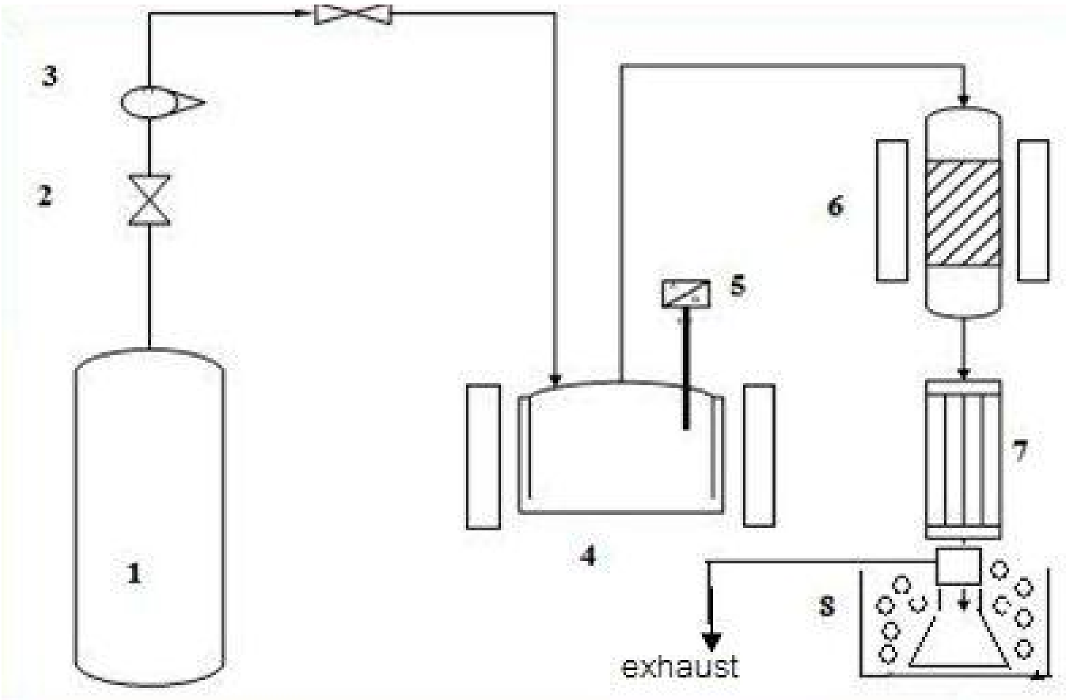

Figure 7 Schematic diagram of experimental setup for pyrolysis of soybean cake:

(1) nitrogen cylinder, (2) valve, (3) mass flow meter, (4) reactor vessel,

(5) thermocouple, (6) packed bed tube reactor with heater, (7) condenser and

(8) ice with salt bath

4. Product Analysis and Characterization

The liquid products from pyrolysis and after upgrading were characterized in terms of high heating value and chemical class composition. High heating value (bio-oil without water) was measured by bomb calorimeter. Chemical composition was classified by extracting of bio-oil from silica gel (pre-treated at 105 °C for 3 h) with n-pentane, toluene and methanol to classify as aliphatic, aromatic and polar respectively. Asphaltene was calculated by difference of total. Each fraction of bio-oil was evaporated by rotary evaporator at boiling point of each fraction (37°C for n-pentane, 110°C for toluene and 65°C for methanol) to separate solvent from bio-oil.

The ultimate analysis and gas chromatography mass spectrometer were performed to determine C, H, O, N, S and chemical composition in both organic and aqueous phases of bio-oil. The ultimate analysis was performed by an elemental analyzer (CHNS 932 determinator LECO-VTF-900 Series).

RESULTS AND DISCUSSION

Thermogravimetric analyzer (TGA)

Soybean cake was analyzed by thermogravimetric analyzer (TGA) at 278-973 K and heating rate is 2 K/min. It started to decompose at 523 K. At 523-673 K, weight loss was 67%wt. At 673-973 K, low weight loss of soybean cake was found 11%wt. It showed that soybean cake had high weight loss at 673 K. From this result, soybean cake was pyrolyzed at 673 K.

Product yield

Pyrolysis of soybean cake at 673K yielded 23.6%wt of solid, 28.4%wt of gas and 48.0%wt of liquid as shown in table 2. The yield of bio-oil from pyrolysis of soybean cake was more than that from rice straw (10 %wt) (Wang *et al.*, 2006), from soybean cake produced by Uzun *et al.* (2006) (38.7 %wt) but less than that from silver birch wood (53.3 %wt) produced by Qian *et al.* (2007).

Different catalysts were used to upgrade the bio-oil in situ.

The yields of solid product and gas product from upgrading using different catalysts and no catalyst at the same temperature (673K) were slightly different, 23.6-24.0%wt of solid and 28.3-29.6%wt of gas (Table 2). The solid yield was almost the same at the same temperature as Wang *et al.* (2006) and Uzun *et al.* (2005) mentioned that solid yields depend on pyrolysis temperature. At higher temperature it was expected to have less solid.

The liquid yield from catalytic process was slightly lower than that from the non-catalyst reaction (48.1%wt of non-catalyst compared with 46.4-48.0%wt of upgrading). Bio-oil from non-catalyst reaction consisted of 37.8%wt of organic phase and 62.2%wt of aqueous phase. The amounts of organic phase and aqueous phase fraction depend on chemicals contained in raw materials and temperature (Putun *et al.*, 1999). Putun et al.(1999) reported that at 673K, 76.6%wt of organic phase and 23.4%wt of aqueous phase were obtained from pyrolysis of sunflower, 58.8%wt of organic phase and 41.2%wt of aqueous phase was obtained from pyrolysis of hazelnut shells and 63.2%wt of organic phase and 36.8%wt of aqueous phase was obtained from pyrolysis of *Euphorbia rigida*. The liquid yield from upgrading by HZSM-5 was less than by MCM-41 due to HZSM-5 produced lighter compound than MCM-41. The acid sites of HZSM-5 was inside restricted cavities therefore, most small molecules which were in gas phase were produced (Sinfrônio *et al.,* 2006). When consider MMZ, the results show that the liquid yield is between microporous and mesoporous material which agree with Sinfrônio *et al. (*2006)'s work.

Table 2 Yield (%wt) of bio-oil, char and gas from soybean pyrolysis with and without catalysts at 673K

Type of upgrading reaction	**bio-oil (% wt)**	**char (% wt)**	**gas (% wt)**
non-catalyst reaction	48.07	23.59	28.41
upgrading by MCM-41	48.02	23.70	28.28
upgrading by HZSM-5	46.79	23.60	29.61
upgrading by MMZ	47.98	23.58	29.34
upgrading by mixed catalysts MCM-41: HZSM-5 = 2: 1 (by weight)	47.73	23.63	28.64
upgrading by mixed catalysts MCM-41: HZSM-5 = 1: 1 (by weight)	46.36	24.01	29.61
upgrading by mixed catalysts MCM-41: HZSM-5 = 1: 2 (by weight)	47.40	23.67	28.93

The upgraded bio-oil consisted of 33.0-35.9 %wt of organic phase and 64.1-67.0%wt of aqueous phase (Table 3) which means that both MCM-41, HZSM-5 did not have effect on the bio-oil yield but on reduction of the amount of the organic phase. The results agreed with those of Adam *et al.* (2006), their amount of the organic phase 17.6%wt of non-catalyst reaction was reduced to 13.1%wt with catalyt and the amount of the aqueous phase increased (from 17.40%wt of non-catalyst reaction to 23.5%wt with catalyst) for upgrading bio-oil by MCM-41. High water content indicates a strong catalytic activity of the catalyst, since water is the product of many catalytic reactions (Aho *et al.*, 2008).

Table 3 Yield (%wt) of organic and aqueous phases of bio-oils from soybean pyrolysis at 673K

Type of bio-oil	**Organic phase (% wt)**	**Aqueous phase (%wt)**
Bio-oil from pyrolysis of soybean cake (non-catalyst)	37.85	62.15
Upgraded bio-oil by MCM-41	34.84	65.16
Upgraded bio-oil by HZSM-5	35.88	64.12
Upgrading by MMZ	34.08	65.92
Upgraded bio-oil by mixed MCM-41:HZSM-5 = 1:1 (by weight)	33.00	67.00
Upgraded bio-oil by mixed MCM-41:HZSM-5 = 2:1 (by weight)	35.54	64.46
Upgraded bio-oil by mixed MCM-41:HZSM-5 = 1:2 (by weight)	33.13	66.87

Elemental analysis

For elemental analysis, soybean cake mainly consists of carbon (45.9%wt), oxygen (42.5%wt), hydrogen (7.5%wt) and nitrogen (3.8%wt) (Table 4). The elements from different raw materials contain different elemental fractions such as cotton stalk (Putun *et al.*, 2005) consists of 48.89%wt of carbon, 5.21%wt of hydrogen, 1.19%wt of nitrogen and 44.71%wt of oxygen, rice straw (Wang et al., 2006) consists of 37.06%wt of carbon, 5.18%wt of hydrogen, 0.84%wt of nitrogen and 56.92%wt of oxygen and soybean cake (Uzun *et al.*, 2006) consists of 55.89%wt of carbon, 6.57%wt of hydrogen, 9.29%wt of nitrogen and 28.25%wt of oxygen. The hydrogen to carbon mole ratio of soybean cake is 1.97 which is higher than 1.47 of corn stalks (Uzun *et al.*, 2009), 1.70 of rice staw (Wang *et al.*, 2007) and 1.41 of soybean cake (Uzun *et al.*, 2006). The oxygen to carbon mole ratios of soybean cake is 0.69 which is close to 0.64 of corn stalks (Uzun *et al.*, 2009) but higher than 0.38 of soybean cake (Uzun *et al.*, 2006). Uzun's soybean cake contains different elemental fractions, compared with soybean cake from this experiment. Uzun's soybean was grown in Turkey while soybean in this study was grown in Thailand.

The element of aqueous phase of the bio-oil consists of 52.8%wt carbon, 35.7%wt oxygen and 7.9%wt hydrogen and the element of organic phase consists of 75.1%wt carbon, 9.0%wt oxygen and 10.1%wt hydrogen. The mole ratios of hydrogen to carbon are 1.79 and 1.61 in aqueous phase of bio-oil and organic phase of bio-oil, respectively. The mole ratios of hydrogen to carbon in bio-oil for both aqueous and organic phases are between bitumen (1.40) and gasoline (1.90) as shown in Table 4. Compared with Uzun's bio-oil soybean cake, the element of organic phase consists of carbon (67.2%wt), oxygen (13.1%wt), hydrogen (9.0% wt) and the mole ratio of hydrogen to carbon is 1.60. There is no difference between the bio-oil in this work and Uzun's bio-oil in term of the mole ratio of hydrogen to carbon but the percent weight of carbon in Uzun's bio-oil is less than the bio-oil of this study (67.2%wt of carbon in Uzun's bio-oil in the organic phase compared with 75.1%wt of carbon in the bio-oil of this study in the organic phase).

The oxygen content of soybean cake was reduced after converting to bio-oil by pyrolysis reaction. The oxygen to carbon mole ratios of organic phase of bio-oil is reduced to 0.09 (87% from raw material). The decrement of the oxygen to carbon mole ratios were also shown in the other work. The oxygen to carbon mole ratios were 0.28 (56% reduction from The oxygen to carbon mole ratio in raw material) for corn stalks (Uzun *et al*., 2009) and 0.15 (61% reduction from The oxygen to carbon mole ratio in raw material) for soybean cake (Uzun *et al*., 2006).

Table 4 Elemental fractions of soybean cake aqueous phase and organic phase of bio-oil produced from soybean cake.

Type of energy source	**C (%wt)**	**H (%wt)**	**N (%wt)**	**S (%wt)**	**O (%wt)**	**O/C (by mole)**	**H/C (by mole)**
Soybean cake	45.940	7.547	3.798	0.203	42.512	0.69	1.97
Aqueous phase	52.839	7.882	3.600	0.001	35.678	0.51	1.79
Organic phase	75.097	10.058	5.716	0.144	8.985	0.09	1.61
Gasoline	-	-	-	-	-	-	1.90[a]
Bitumen	-	-	-	-	-	-	1.40[a]

[a] **Source:** Huber (2006)

Pyrolysis and upgrading

High heating value

High heating value of bio-oil from pyrolysis, after upgraded by MCM-41, HZSM-5 and the blend of MCM-41 and HZSM-5 with the mole ratio of 1:1, 1:2 and 2:1 were measured by bomb calorimeter. Upgraded bio-oils had higher high heating value than that from non-catalyst reaction for organic phase. The high heating value increased from 19.9 MJ/kg to 36.6-38.5 MJ/kg **(**Figure8). Upgraded bio-oils by the blend of MCM-41 and HZSM-5 with the ratio of 1:1 has the highest high heating value for organic phase (38.5 MJ/kg) and the upgraded bio-oil blend of MCM-41 and HZSM-5 with the ratio of 2:1 has the lowest heating value (36.6 MJ/kg).

MCM-41 showed better performance than HZSM-5 and MMZ for organic phase for the higher heating value (38.5 MJ/kg from MCM-41 compared with 36.8 MJ/kg from HZSM-5). Upgraded bio-oil by all the catalysts improved high heating value around 14.6-18.6 MJ/kg (by 73-93% compared with non-catalyst reaction). Compared with the wok of Uzun *et al.* (2009) the high heating value of bio-oil from pyrolysis of corn stalk (29.7 MJ/kg) increased to 33.3 MJ/kg by HZSM-5. High heating value from Uzun's upgraded bio-oil was improved only 3.6 MJ/kg (by 12% compare with non-catalyst reaction).

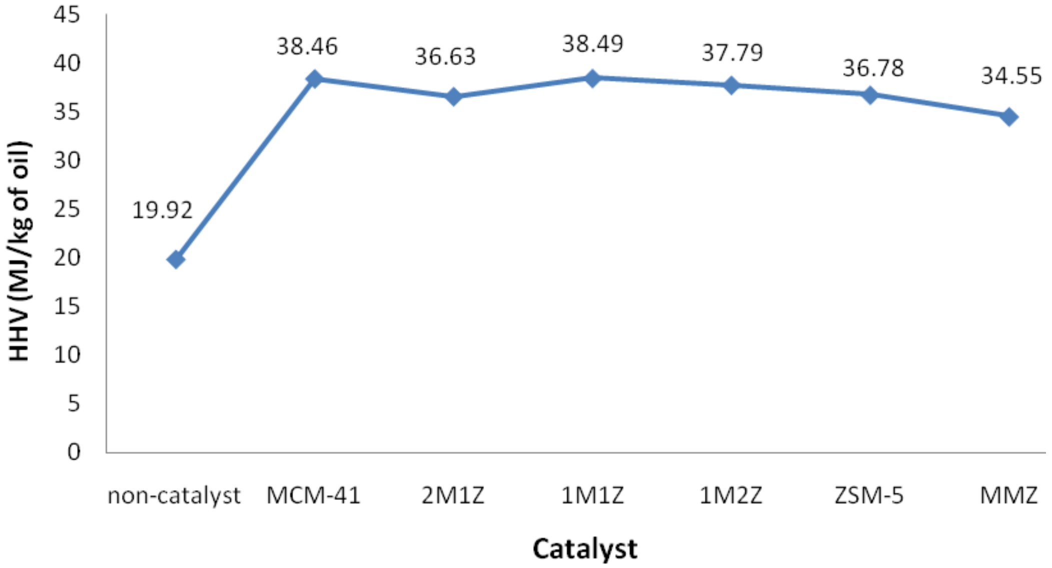

Figure 8 High heating values (HHV) (MJ/kg) of bio-oil from non-catalyst reaction and bio-oil upgraded by MCM-41, HZSM-5, MMZ and the blend of MCM-41 and HZSM-5 with the ratios of 1:1 (1M1Z), 1:2(1M2Z) and 2:1(2M1Z) for organic phase.

Upgrading by both catalysts did not improve aqueous phase property and also decreased high heating value from 5.54 MJ/kg for non-catalyst to 4.20-4.58 MJ/kg for upgraded bio-oils. Upgraded bio-oil by the blend of MCM-41 and HZSM-5 with the ratio of 1:1 has the highest heating value for aqueous phase (4.58 MJ/kg) and upgraded bio-oil by MCM-41 has the lowest heating value (4.20 MJ/kg). HZSM-5showed better performance than MCM-41 for aqueous phase (4.46 MJ/kg from upgraded bio-oil by HZSM-5 compared with 4.20 MJ/kg from upgraded bio-oil by MCM-41) **(**Figure9).

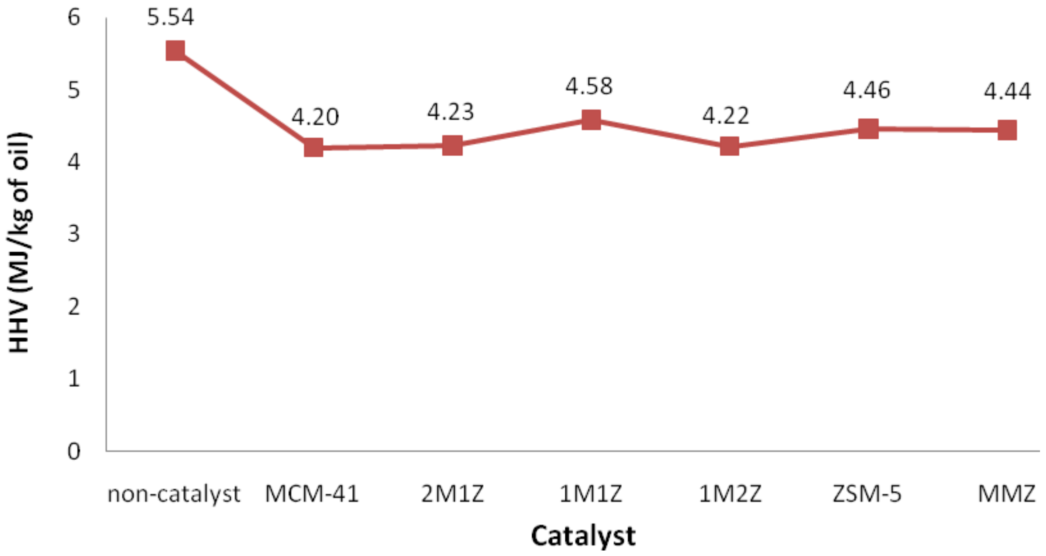

Figure 9 High heating values (HHV) (MJ/kg) of bio-oil from non-catalyst reaction and bio-oil upgraded by MCM-41, HZSM-5 and the blend of MCM-41 and HZSM-5 with the ratios of 1:1 (1M1Z), 1:2(1M2Z) and 2:1(2M1Z) for aqueous phase.

High heating value of bio-oil increased after it was upgraded by catalyst. Catalyst had changed the mechanism of thermal cracking from the cleavage in the terminal group of hydrocarbon chain to random cleavage (Sinfrônio *et al.,* 2006). The cleavages in the terminal groups produce a large amount of small molecules and big molecules (10-35 and 80-120 atom mass unit) in Sinfrônio *et al*.(2006)'s work while random cleavage, the small molecules from terminal groups do not occur. The molecule size was limited by the restricted channel and pore volume of the catalyst. This reason can describe how MCM-41 shows the best result among others. It has bigger pore size than HZSM-5 therefore the products from upgrading by MCM-41 are in the bigger size range than those of HZSM-5 (C3-C6 for HZSM-5 and C4-C8 for

MCM-41 in Sinfrônio *et al*. (2006)'s work). Mixed catalyst also contains HZSM-5 and MCM-41, the soybean cake cracking of HZSM-5 into smaller molecules has reduced the high heating value of bio-oil. For MMZ, the high heating value was lower than those of MCM-41 and HZSM-5 due to its disorder structure (Hyung *et al*., 2008) and diffusional limitation for the access of the reactant molecules to the acidic sites of the catalyst (Sinfrônio *et al.,* 2006).

For aqueous phase, the reduction of high heating value may due to the cleavage of hydrocarbon chain of molecules which may dissolve in aqueous phase of bio-oil.

Chemical class composition

Chemical class compositions of bio-oils were classified into aliphatic, aromatic, polar and asphaltene fractions to indicate the effect of catalysts on bio-oil. Increasing of aliphatic fraction due to upgrading of bio-oil by MCM-41, HZSM-5, MMZ and the blend was observed. The blend of MCM-41 and HZSM-5 with the ratio of 2:1 has the highest aliphatic fraction 52.9%wt and the blend of MCM-41 and HZSM-5 with the ratio of 1:1 has the least aliphatic fraction 38.4%wt but it is still higher than that from non-catalyst reaction (29.1%wt) **(**Figure10).

Aromatic fraction significantly decreased for upgraded bio-oil from 18.4 %wt of non-catalyst to 6.4-15.1 %wt. The catalyst which reduced aromatic fraction the most is the blend of MCM-41 and HZSM-5 with the ratio of 2:1(6.4%wt aromatic fraction) and MCM-41 reduced aromatic fraction the best (10.9%wt aromatic fraction) **(**Figure11).

Both MCM-41 and HZSM-5 did not have much effect on polar fraction except MMZ because the amount of polar fraction of upgraded bio-oil from all catalysts did not change significantly (31.2 %wt of non-catalyst compared to 22.9-30.8 %wt of upgraded bio-oil). Especially, upgraded bio-oil by HZSM-5 seems to have the least effect on polar fraction (reduced from 31.2%wt to 30.8%wt) **(**Figure12).

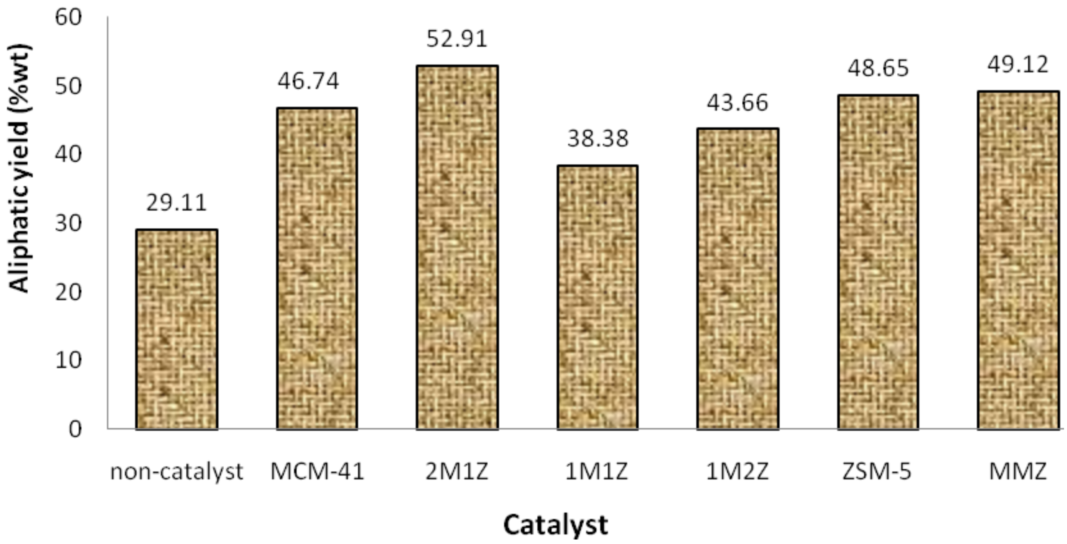

Figure 10 Aliphatic fraction in the organic phase of bio-oil (%wt) from non-catalyst reaction and bio-oil upgraded by MCM-41, HZSM-5, MMZ and the blend of MCM-41 and HZSM-5 with the ratios of 1:1 (1M1Z), 1:2(1M2Z) and 2:1(2M1Z)

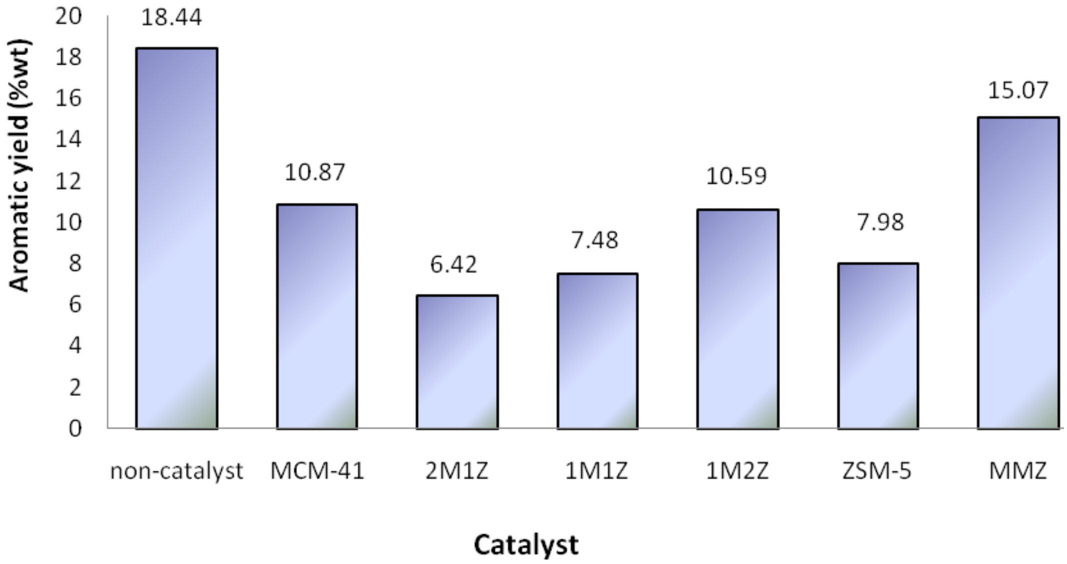

Figure 11 Aromatic fraction in the organic phase of bio-oil (%wt) from non-catalyst reaction and bio-oil upgraded by MCM-41, HZSM-5, MMZ and the blend of MCM-41 and HZSM-5 with the ratios of 1:1 (1M1Z), 1:2(1M2Z) and 2:1(2M1Z)

Asphaltene

Asphaltene is defined as the residue from extraction of aliphatic, aromatic and polar. It can be long chain hydrocarbon, complex hydrocarbon or else. Upgraded bio-oil by different catalysts and the catalyst blend with different ratios yielded different amounts of asphaltene. Asphaltene fraction in bio-oil decreased when the bio-oil were upgraded by MCM-41, HZSM-5 and the blend of MCM-41 and HZSM-5 with the ratio of 2:1 from 21.2%wt of non-catalyst reaction to 12.6-17.2%wt of upgraded bio-oil. However, asphaltene fraction in bio-oil did not change for the blend of MCM-41 and HZSM-5 with the ratio of 1:2 (22.8%wt) and also increased for the ratio of 1:1 (26.6%wt) **(**Figure13).

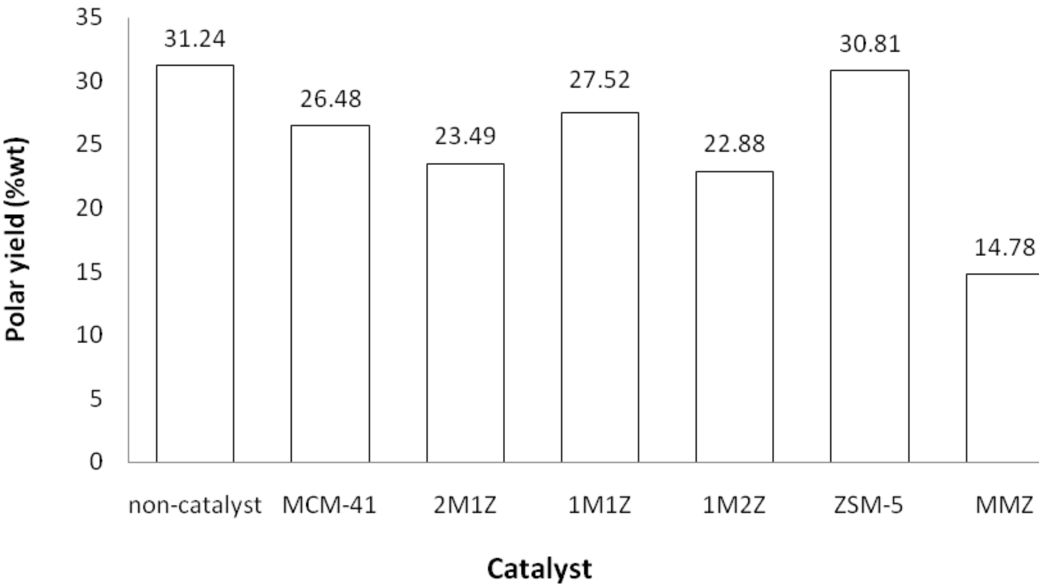

Figure12 Polar fraction in the organic phase of bio-oil (%wt) from non-catalyst reaction and bio-oil upgraded by MCM-41, HZSM-5, MMZ and the blend of MCM-41 and HZSM-5 with the ratios of 1:1 (1M1Z), 1:2(1M2Z) and 2:1(2M1Z)

The chemical composition from each catalyst and ratio is different. For MMZ, the chemical composition is similar to the blend of MCM-41 and HZSM-5 with the ratio of 1:2 but bio-oil from MMZ contains higher aliphatic and aromatic and lower polar and asphaltene than MCM-41:HZSM-5 = 1:2.

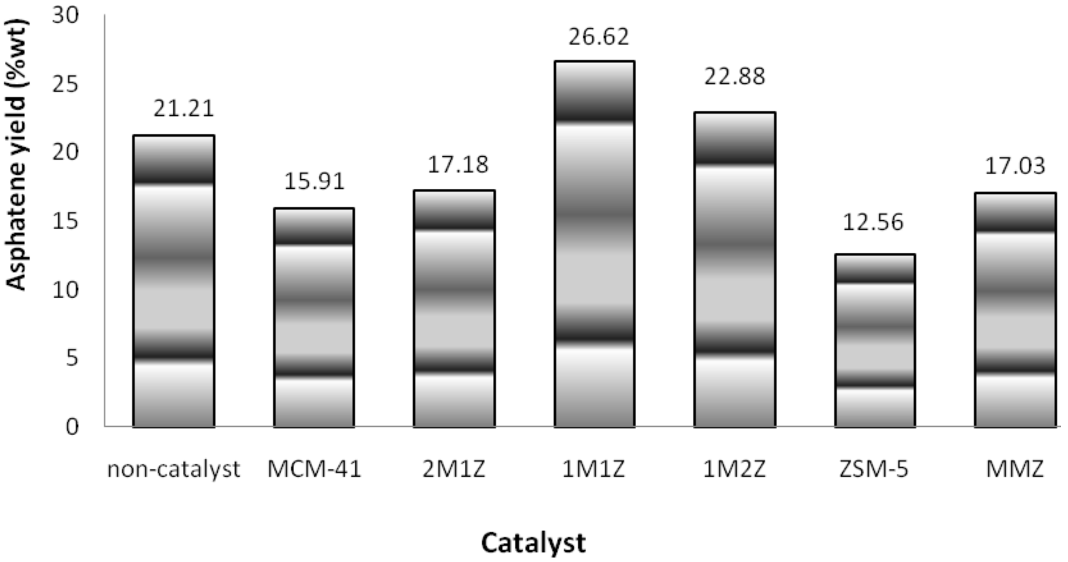

Figure13 Asphaltene fraction in the organic phase of bio-oil (%wt) from non-catalyst reaction and bio-oil upgraded by MCM-41, HZSM-5, MMZ and the blend of MCM-41 and HZSM-5 with the ratios of 1:1 (1M1Z), 1:2(1M2Z) and 2:1(2M1Z)

The change of chemical class composition can be described through the mechanism of thermal cracking. During thermal cracking, the carbenium ion species (R_3C^+) were formed from the cleavage of hydrocarbon chain. Once they were formed, they could be subject to a wide number of reactions, including β-cracking, hydride transfer, isomerization, cyclization and aromatization, therefore, a large range of compounds were produced almost at the same time during the degradation process (Sinfrônio *et al.,* 2006). Cracking catalyst such as MCM-41 and HZSM-5 have changed cleavage position from terminal group to random position, therefore, complex molecules which dissolve in aromatic and asphaltene fraction can be cracked to aliphatic fraction. The different ratios of catalyst mixing may change reaction mechanism due to each catalyst has different selectivity, therefore, bio-oils from different ratios have different chemical class compositions. However, when compared with no catalyst they all had increases of aliphatic fraction and decreases of other fractions except the ratio of 1:1 which the asphaltene fraction as well as the high heating value increased slightly **(**Figures13 and 8). The sequence of packing may affect the reaction mechanism and differ product properties so the effect of sequence of catalysts packing was analysed in this study.

Total energy output of liquid products for both phases were calculated by multiplying liquid yield of each batch (kg of oil/kg of biomass) (Table 3,4) by its high heating value (MJ/kg of oil) (Figure 7). For organic phase, upgraded bio-oil has higher high heating value than the nonupgraded one (3.62MJ/kg of non-catalyst compared to 5.65-6.43 MJ/kg of upgraded bio-oil). MCM-41 gave the highest high heating value (6.43MJ/kg of biomass) **(**Figure14) followed by HZSM-5 (6.17MJ/kg of biomass), MMZ and the blend catalyt for all ratios provided lower heating values.

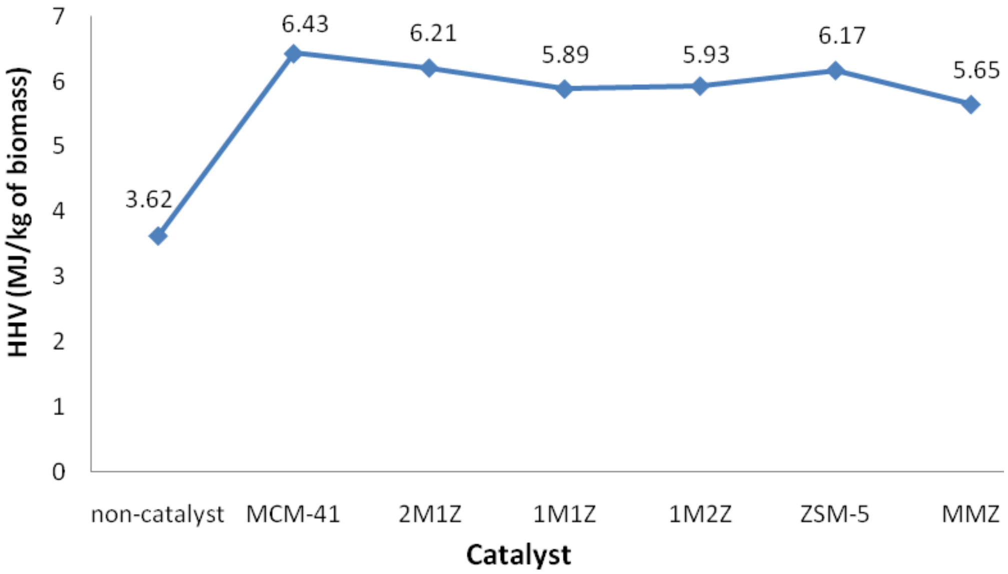

Figure 14 Total energy output for the organic phase of bio-oil (MJ/kg of biomass) from non-catalyst reaction and bio-oil upgraded by MCM-41, HZSM-5, MMZ and the blend of MCM-41 and HZSM-5 with the ratios of 1:1 (1M1Z), 1:2(1M2Z) and 2:1(2M1Z)

Total energy output for aqueous phase shows opposite result from the organic phase by decrement of high heating value of the upgraded bio-oil (from 1.66MJ/kg of biomass for non-catalyst to 1.30-1.42 MJ/kg of biomass for the upgraded bio-oil).

The blend of MCM-41 and HZSM-5 with the ratio of 2:1 provided the lowest high heating value for aqueous phase **(**Figure15).

Total energy output from the two phases, of all upgraded bio-oils were higher than that from non-catalyst reaction. Bio-oil upgraded by MCM-41 gave the highest output energy (7.75MJ/kg of biomass) among all the catalysts in this study (Figure16).

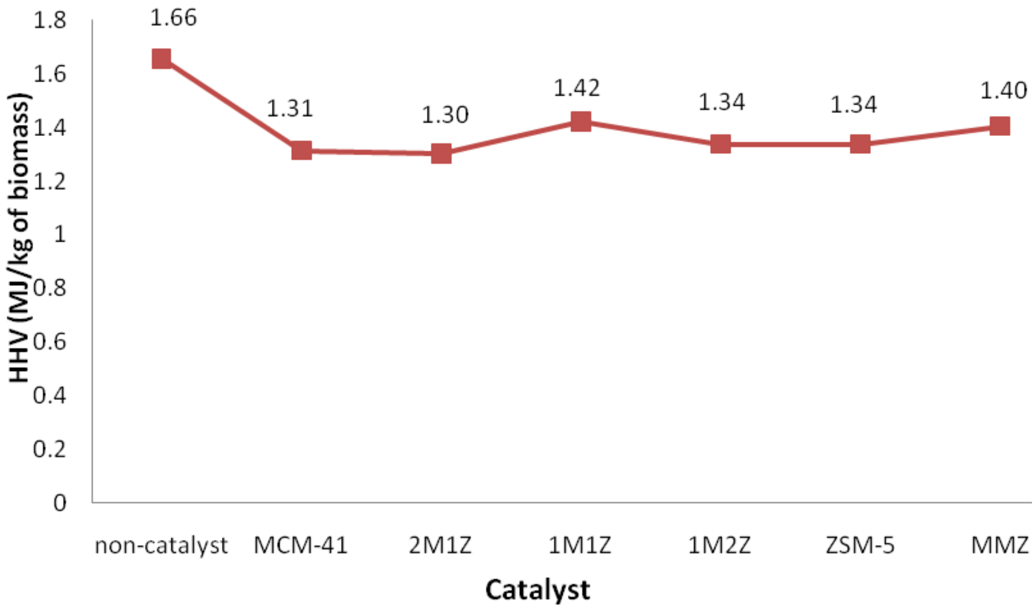

Figure 15 Total energy output for the aqueous phase of bio-oil (MJ/kg of biomass) from non-catalyst reaction and bio-oil upgraded by MCM-41, HZSM-5, MMZ and the blend of MCM-41 and HZSM-5 with the ratios of 1:1 (1M1Z), 1:2(1M2Z) and 2:1(2M1Z)

The effect of sequence of catalysts packing

From the results of upgrading of bio-oil by MCM-41, HZSM-5 and the blends of both catalysts with different ratios, MCM-41 showed the best performance in terms of high heating value (MJ/kg of oil)(Figure 8) and total energy output of bio-oil (MJ/kg of biomass) (Figure 16). The blend of both catalysts did not increase high heating value and total energy output of bio-oil which may due to the sequence of catalysts packing.

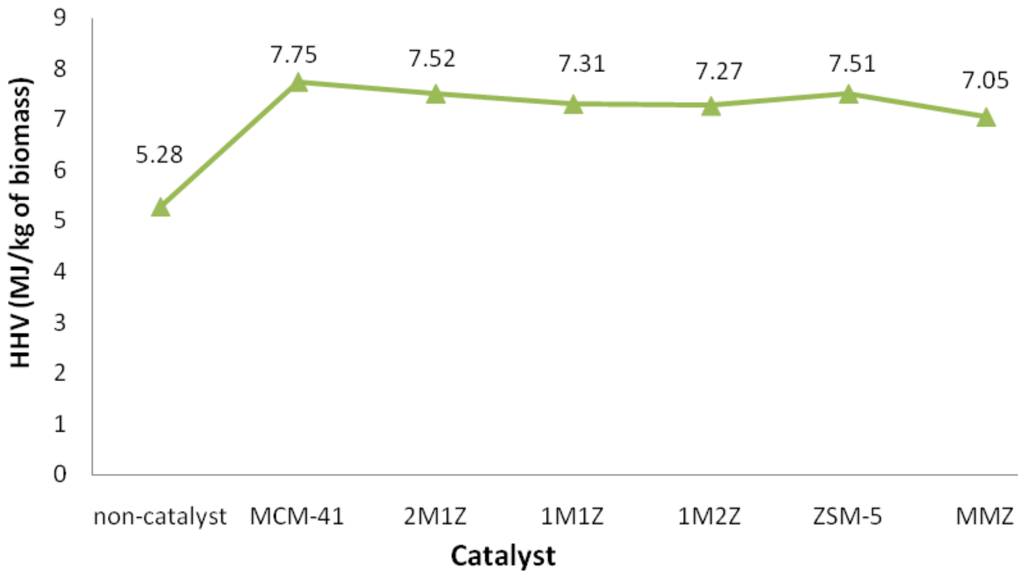

Figure 16 Total energy output from bio-oils (both of organic and aqueous phases) from non-catalyst reaction and bio-oil upgraded by MCM-41, HZSM-5, MMZ and the blend of MCM-41 and HZSM-5 with the ratios of 1:1 (1M1Z), 1:2(1M2Z) and 2:1(2M1Z)

Mixed catalysts of MCM-41 and HZSM-5 with different packing methods may have effect on bio-oil for both quantity and quality. The following two methods of packing were selected to investigate the effect of packing method: order packing and random packing.

Order packing is done by packing MCM-41 in front of HZSM-5 (Figure 17) because vapor phase from pyrolysis of biomass contains long chain hydrocarbon which is a big molecule and may not enter small pore size like HZSM-5, therefore, MCM-41 which is mesoporous material which having bigger pore size than microporous HZSM-5 seems to be an appropriate one to cracking big molecule into smaller molecule. Then, small molecules enter HZSM-5 which has higher activity to convert long chain hydrocarbon into more valuable oil.

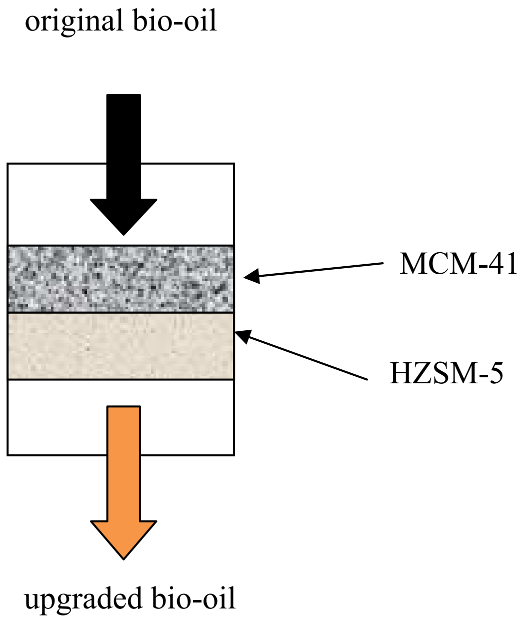

Figure 17 Order packing of MCM-41 followed by HZSM-5 in a pack bed tube reactor

Random packing is done by mixing both MCM-41 and HZSM-5 without concerning the order of packing. The large molecule may be cracked by MCM-41 yielding smaller molecule which is cracked further by HZSM-5 nearby.

The blend of MCM-41 and HZSM-5 with the ratio of 1:1 was chosen to investigate the effect of mixing because this ratio showed the best performance in term of improved high heating value of bio-oil.

In term of liquid yield, order mixing and random mixing give almost the same amount of bio-oil 46.4%wt and 46.0, respectively as well as the amounts of organic phase and aqueous phase in bio-oil (Table 5).

The effect of sequence of catalysts packing were considered in terms of high heating value, the results showed that sequence of catalysts packing have slightly effect on high heating value for organic phase of bio-oil. Upgraded bio-oil from order packing has slightly higher high heating value than another (38.49MJ/kg) (Figure 18).

Table 5 Yield (%wt) of liquid product and the fraction of organic and aqueous phases of upgraded bio-oils by the blend of MCM-41 and HZSM-5 with the ratio of 1:1 with difference sequence of catalysts packing at 673K.

Type of bio-oil	**Bio-oil yield (% wt)**	**Organic phase (% wt)**	**Aqueous phase (% wt)**
order mixing	46.36	33.00	67.00
random mixing	46.01	33.42	66.58

The highest high heating value of the aqueous phase of upgraded bio-oil was obtained by order packing (4.58MJ/kg). The same trend was also observed in organic phase of bio-oil. Order packing did not showed better performance than random packing (Figure 18).

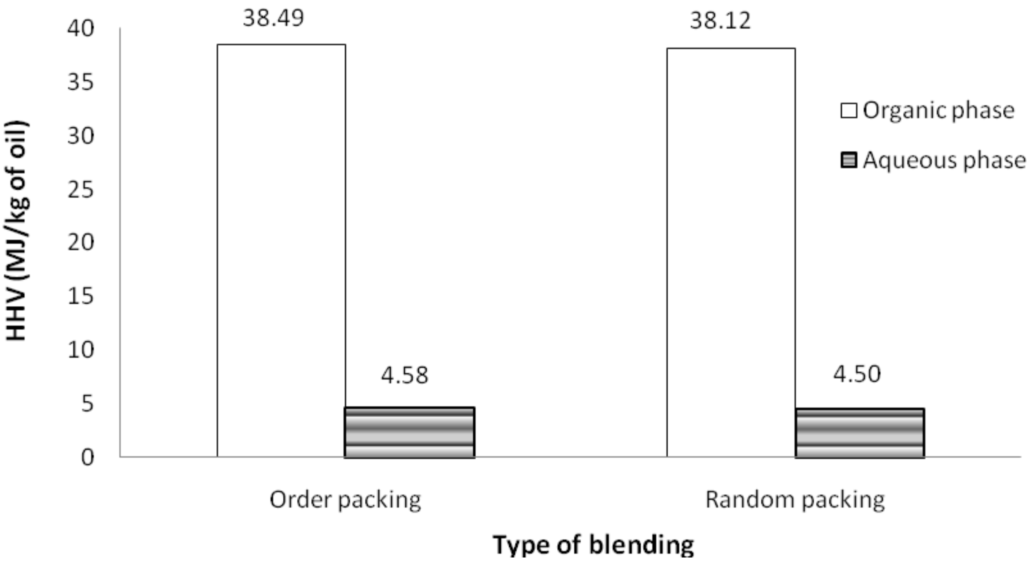

Figure 18 High heating values (HHV) (MJ/kg) of bio-oils upgraded by different sequences of catalysts packing; order packing, random packing and order packing of MMZ with MCM-41

Random packing has less high heating value than the order one. The sequence of cracking reaction may affect some big molecules which cannot reach the acid sites of HZSM-5 which is a microporous material (diameter less than 2 nm) therefore some big molecules left without cracking reaction.

The sequence of catalysts packing showed a slight effect on high heating value therefore the effect of sequence of catalysts packing can be ignored.

When considered in terms of chemical class composition, the sequence of catalysts packing did not have much effect on bio-oil composition because all methods showed the same trend by increasing of aliphatic and asphaltene fractions and decreasing the others (Figures 19).

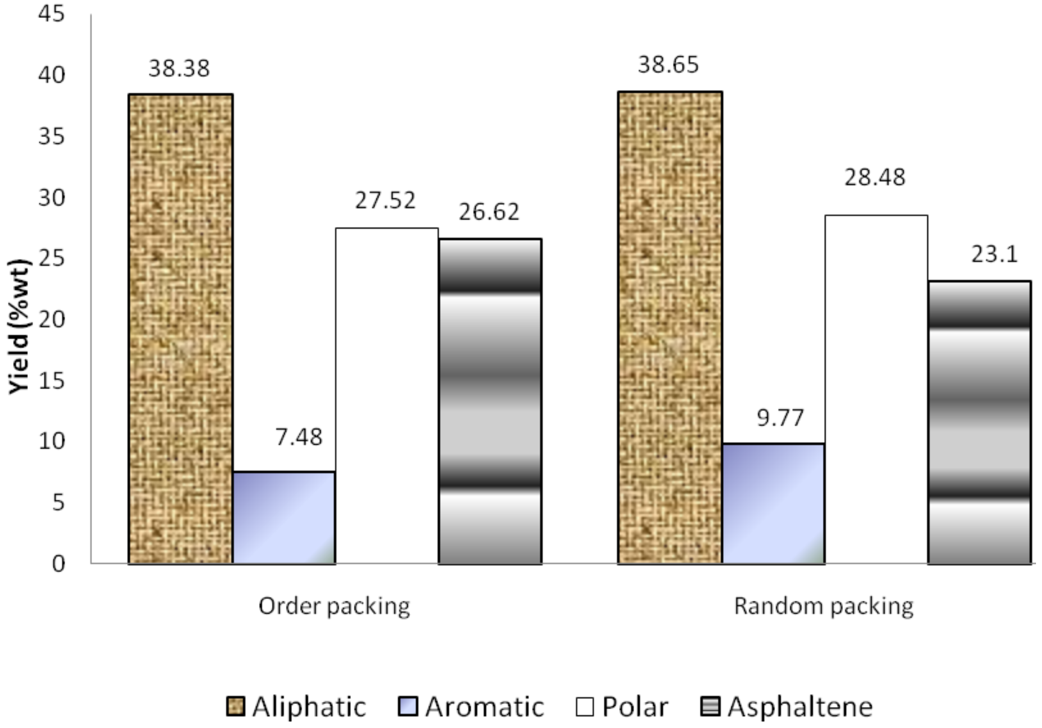

Figure 19 Chemical class composition from organic phases of bio-oils upgraded by different sequences of catalysts packing; order packing and random packing

In terms of total energy output for organic phase which was calculated from the product yield and high heating value. It clearly showed that the sequence of catalysts packing did not have significant effect due to total energy outputs are the same for both phases (Figure 20).

From the results of high heating value, chemical class composition and total energy output, it could be concluded that the sequence of catalysts packing did not have effect on reaction mechanism.

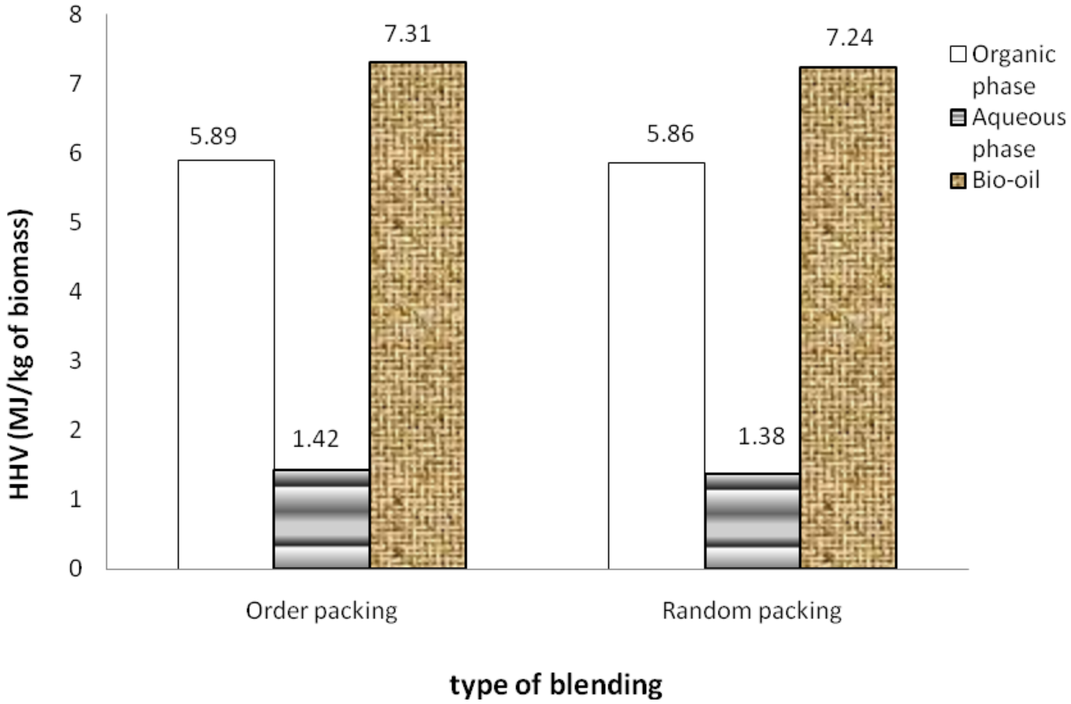

Figure 20 Total energy output of bio-oils upgraded by different sequences of catalysts packing; order packing and random packing

Effect of temperature

Three upgrading temperatures were chosen to investigate the effect of temperature; 623, 673 and 723K. The liquid yield was different when upgrading temperature was changed. The liquid yield increased when upgrading temperature increased due to more raw material was converted to vapor. The highest yield (49.74%wt) was obtained from the highest upgrading temperature (723K) but the highest amount of organic phase (35.67%wt) was obtained from the lowest temperature (623K) (Table 6).

Table 6 Yields (%wt) of liquid product and the fractions of organic and aqueous phases of bio-oils upgraded by MCM-41 at different temperatures; 623, 673 and 723K.

Upgrading temperature	Yield (% wt)	organic phase (% wt)	aqueous phase (% wt)
non-catalyst at 673K	48.07	37.85	62.15
Upgraded by MCM-41 at 623K	45.13	35.67	64.33
Upgraded by MCM-41 at 673K	48.02	34.84	65.16
Upgraded by MCM-41 at 723K	49.74	34.98	65.02

In terms of high heating value, upgrading temperature of 673K seems to be an appropriate temperature because the highest high heating value of bio-oil from organic phase (38.46MJ/kg) was obtained at this temperature (Figure21). The highest high heating value of bio-oil from aqueous phase (4.44MJ/kg) was obtained at 623K (Figure22).

In terms of chemical class composition, when upgrading temperature was increased, aliphatic fraction increased (no difference between 673 and 723K), aromatic fraction decreased, polar fraction increased and asphaltene fraction increased (figures23-26).

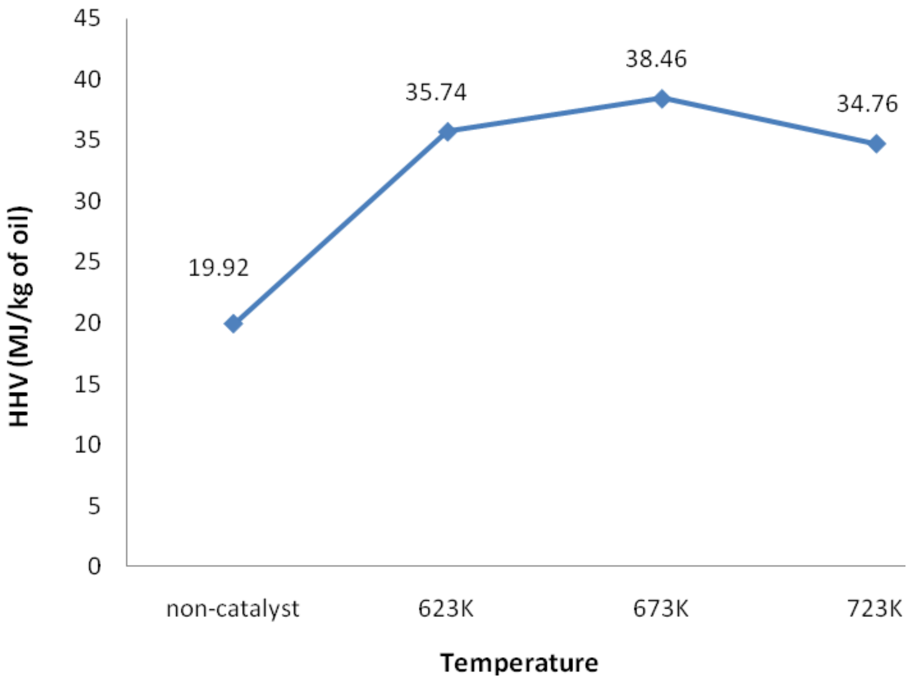

Figure 21 High heating values (HHV) (MJ/kg) of organic phase of bio-oils upgraded by different temperatures; 623, 673 and 723K

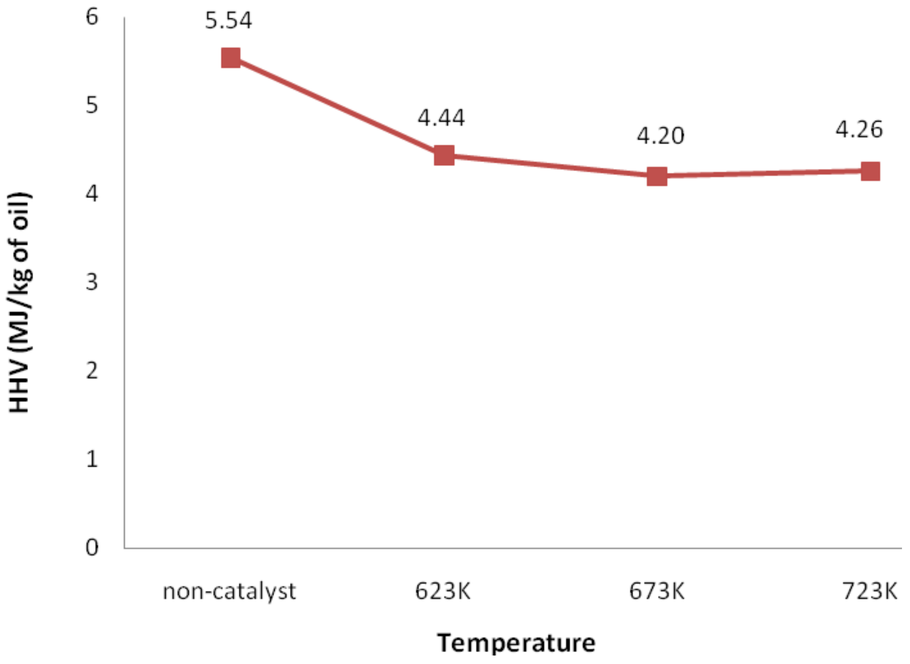

Figure 22 High heating values (HHV) (MJ/kg) of aqueous phase of bio-oils upgraded by different temperatures; 623, 673 and 723K

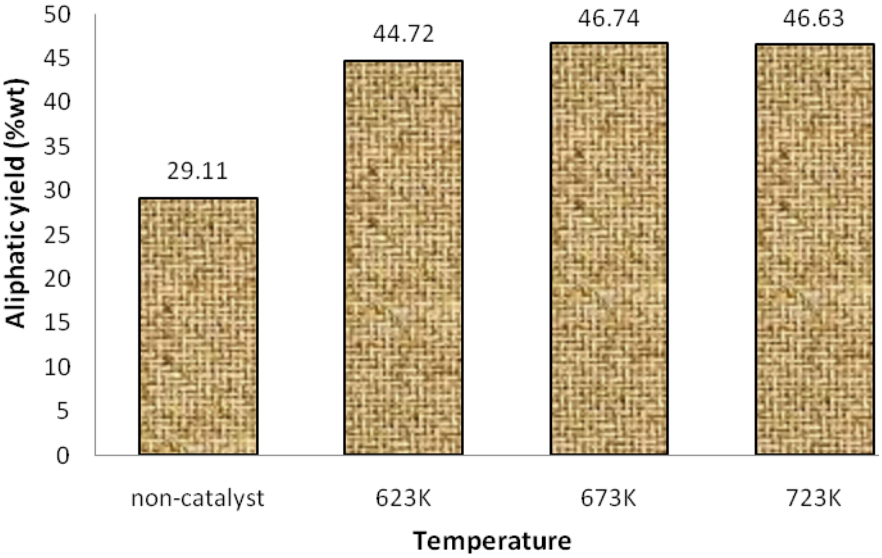

Figure 23 Aliphatic fractions (%wt) from organic phases of bio-oils upgraded by different temperatures; 623, 673 and 723K

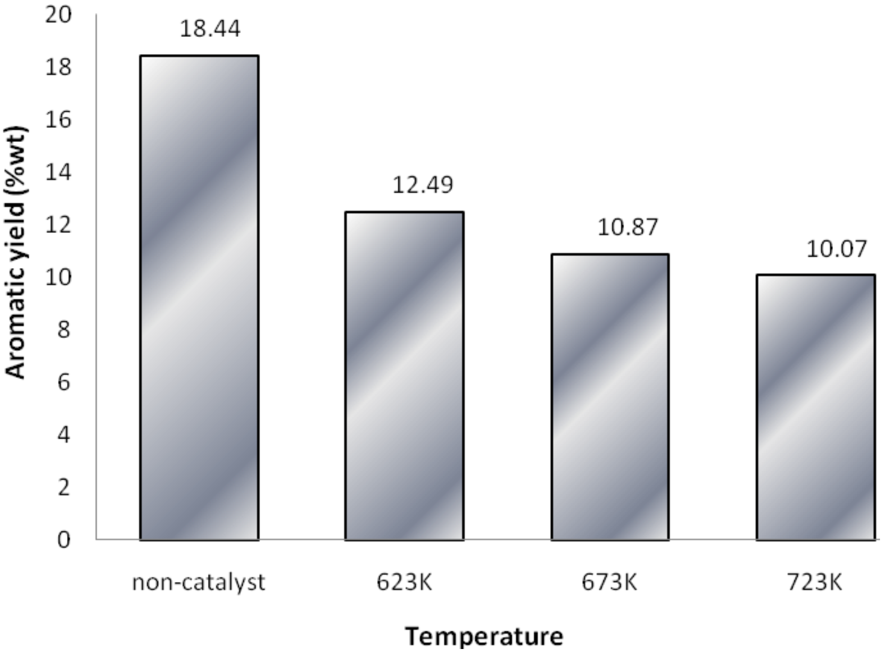

Figure 24 Aromatic fractions (%wt) from organic phases of bio-oils upgraded by different temperatures; 623, 673 and 723K

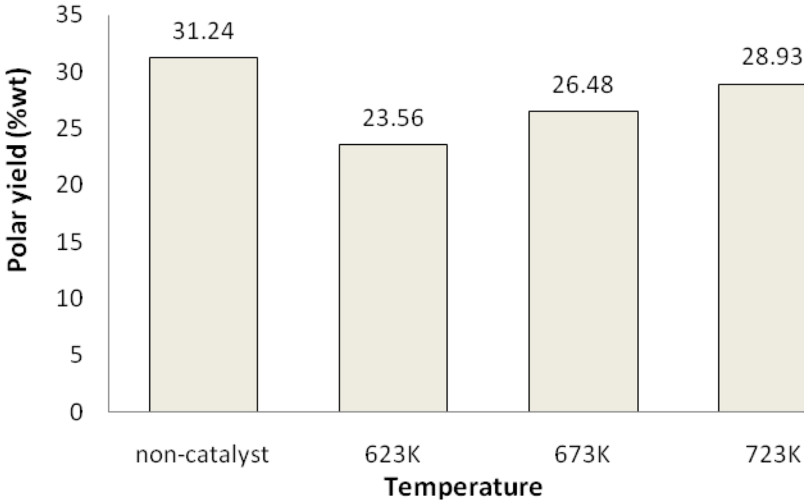

Figure 25 Polar fractions (%wt) from organic phases of bio-oils upgraded by different temperatures; 623, 673 and 723K

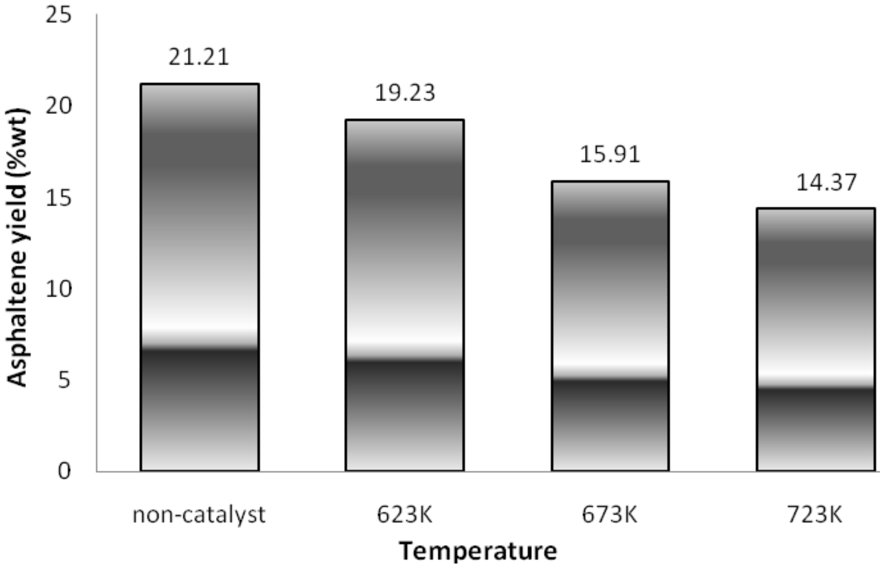

Figure 26 Asphaltene fractions (%wt) from organic phases of bio-oils upgraded by different temperatures; 623, 673 and 723K

In terms of total energy output, 673K is the optimum temperature which provides the highest total energy for organic phase (6.43MJ/kg of biomass) (Figure27) for aqueous phase (1.38MJ/kg of biomass) (Figure 28) and for bio-oil (both organic and aqueous phases) (7.75MJ/kg of biomass) (Figure 29).

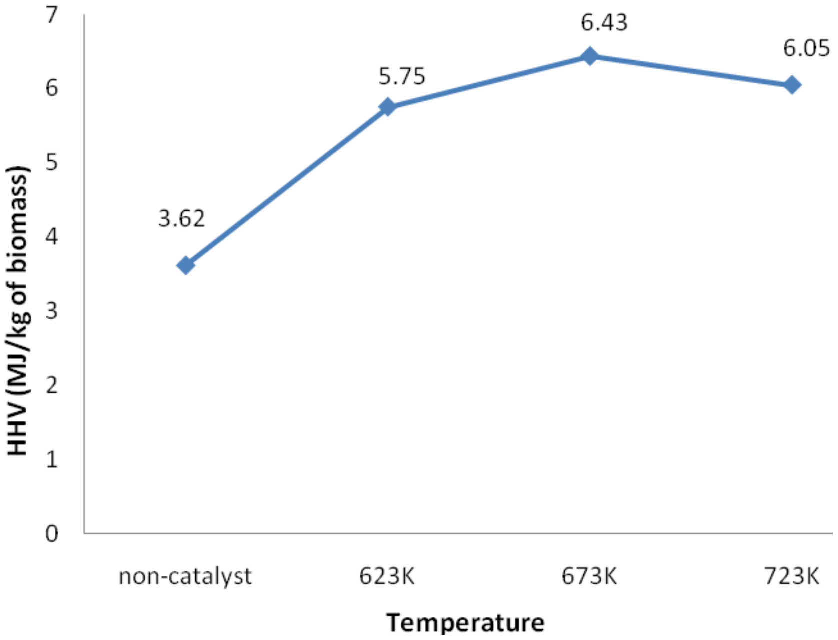

Figure 27 Total energy output (MJ/kg of biomass) of organic phase of bio-oils upgraded at different temperatures; 623, 673 and 723K

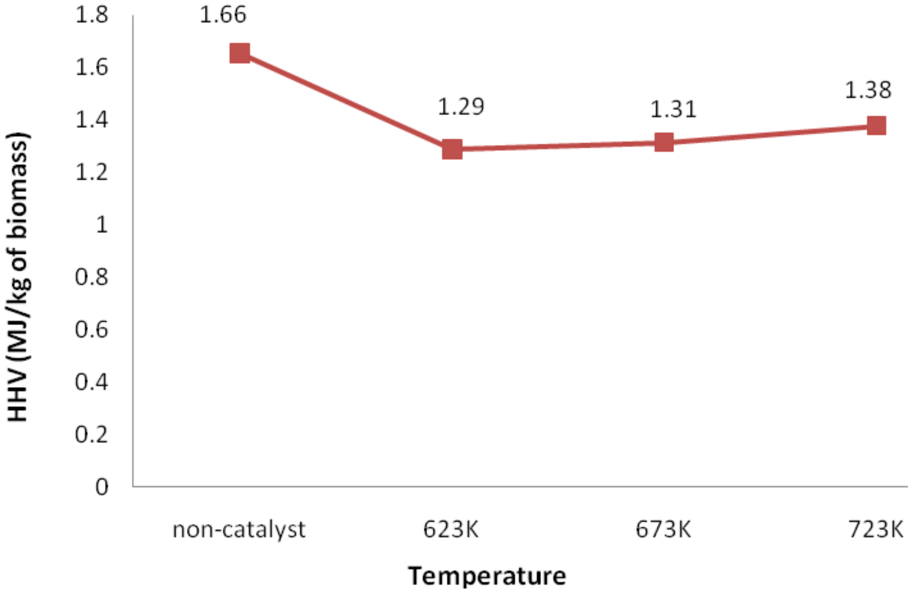

Figure 28 Total energy output (MJ/kg of biomass) of aqueous phase of bio-oils upgraded at different temperatures; 623, 673 and 723K

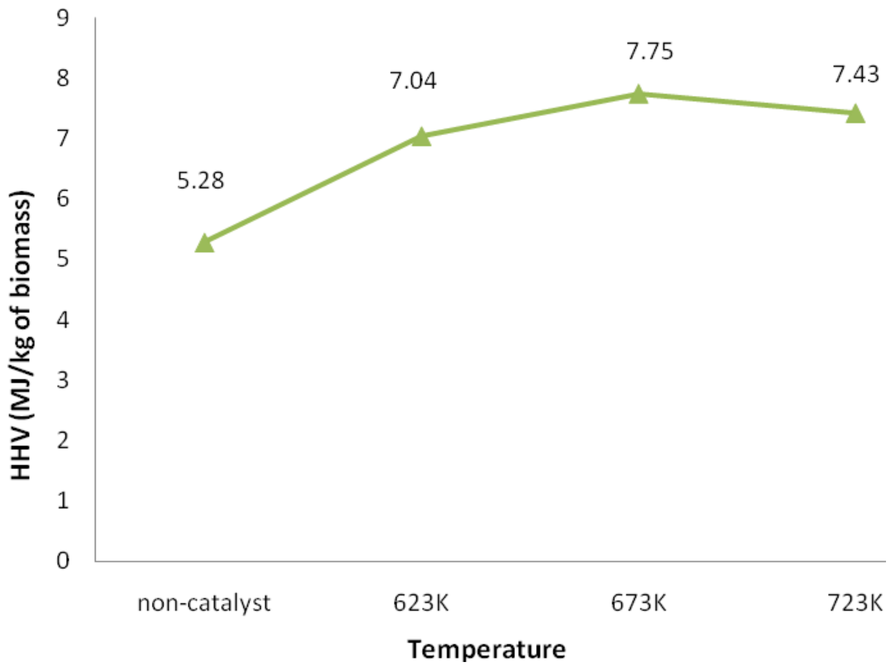

Figure 29 Total energy output (MJ/kg of biomass of bio-oils (both of organic and aqueous phase) upgraded at different temperatures; 623, 673 and 723K

Catalyst regeneration

Both MCM-41 and HZSM-5 were investigated their activities after it was regenerated four times by heating at 773K in the presence of air for 6 hours.

MCM-41 regeneration

The liquid yield (%wt) slightly decreased for regenerated MCM-41 compared with fresh MCM-41 and organic phase also decreased (Table7). In terms of high heating value, first and second regeneration MCM-41 did not have any effect on high heating value in both phases (around 38.5MJ/kg). The high heating value of upgraded bio-oil from the third and the fourth regenerated MCM-41 (34.5-35.9MJ/kg) are different from the fresh MCM-41(38.5MJ/kg) (Figures 30 and 31) therefore MCM-41 seems to be appropriated for regenerated twice only.

Table 7 Yield (%wt) of liquid product and the fractions of organic and aqueous phases of bio-oils upgraded by fresh and regenerated MCM-41 at 673K

Time of regeneration	Yield (% wt)	organic phase (% wt)	aqueous phase (% wt)
non-catalyst	48.07	37.85	62.15
MCM-41	48.02	34.84	65.16
regeneration 1	48.12	34.72	65.28
regeneration 2	47.97	34.91	65.09
regeneration 3	48.01	34.54	65.46
regeneration 4	47.89	34.01	65.99

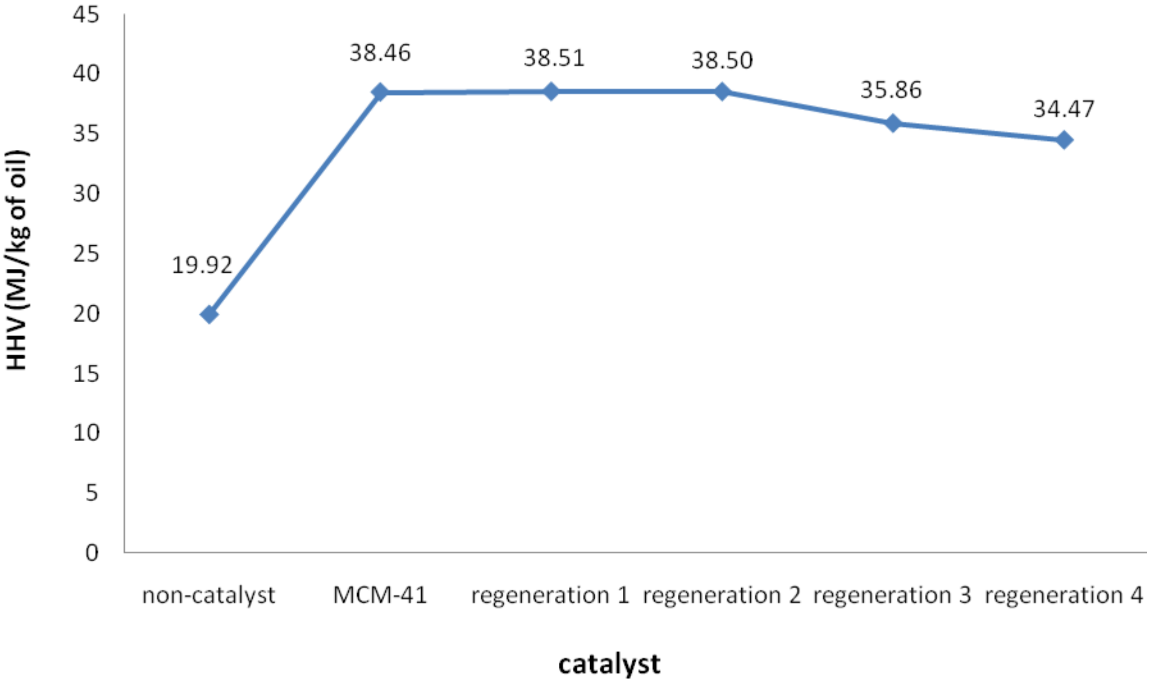

Figure 30 High heating values (HHV) (MJ/kg) of organic phase of bio-oils upgraded by fresh and regenerated MCM-41 at 673K

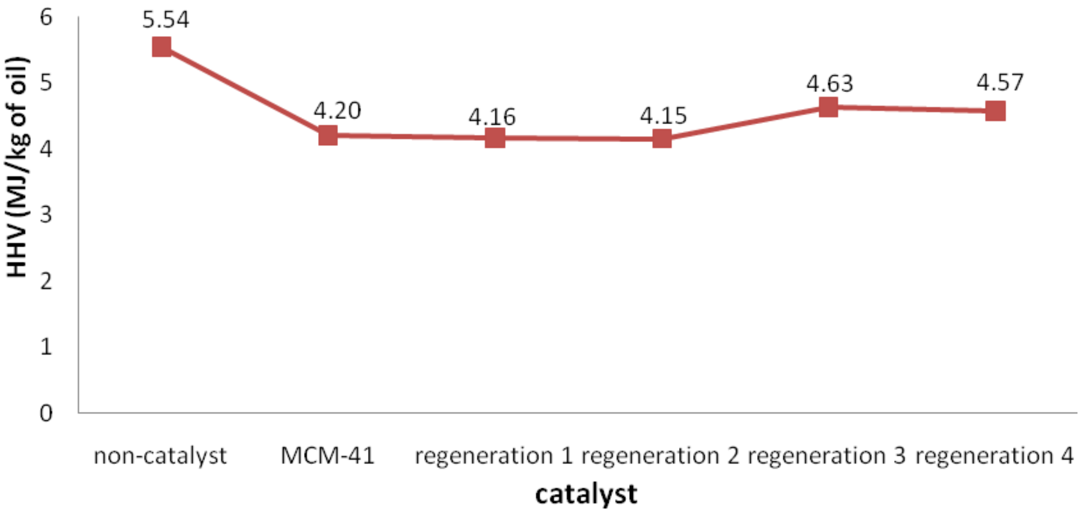

Figure 31 High heating values (HHV) (MJ/kg) of aqueous phase of bio-oils upgraded by fresh and regenerated MCM-41 at 673K

In term of chemical class composition, bio-oils upgraded by regenerated MCM-41 has unstable property by the change of chemical composition.When MCM-41 was regenerated further, aliphaltic fraction decreased (Figure 32), aromatic fraction increased (Figure 33), polar fraction decreased (Figure 34) and asphaltene fraction increased (Figure 35).

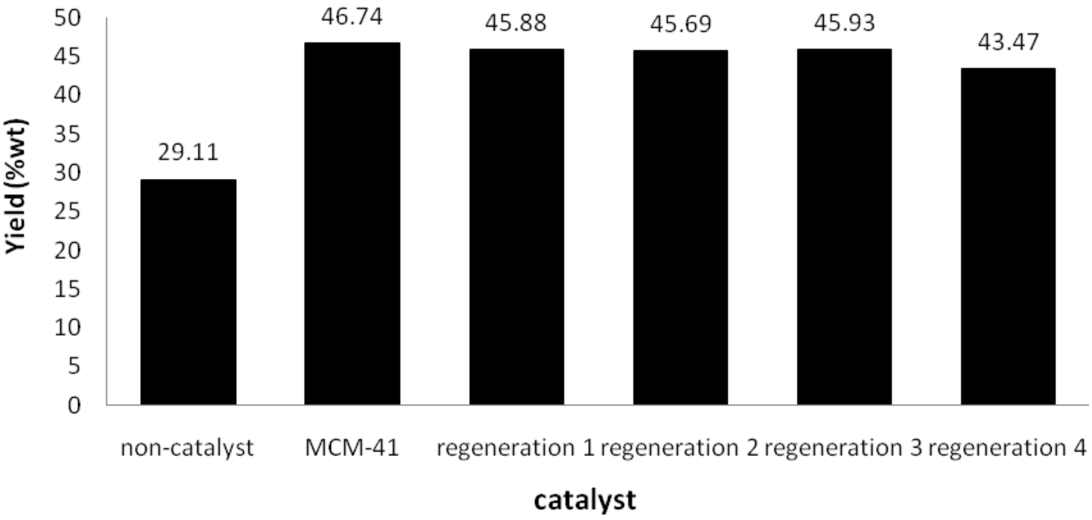

Figure 32 Aliphatic fraction (%wt) of organic phase of bio-oils upgraded by fresh and regenerated MCM-41 at 673K

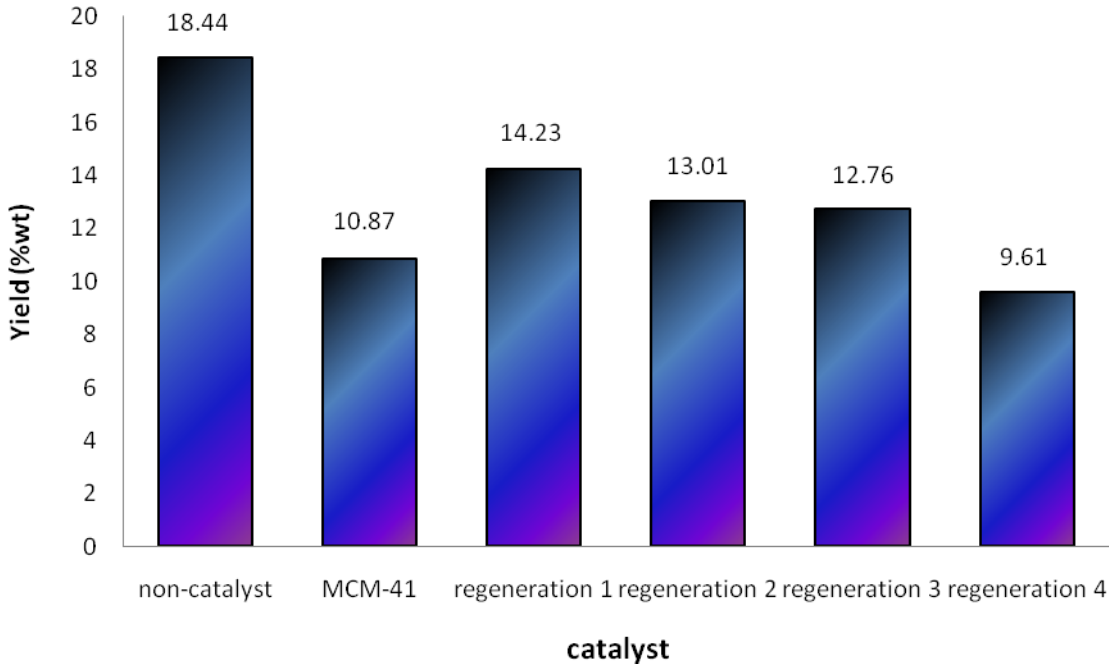

Figure 33 Aromatic fraction (%wt) of organic phase of bio-oils upgraded by fresh and regenerated MCM-41 at 673K

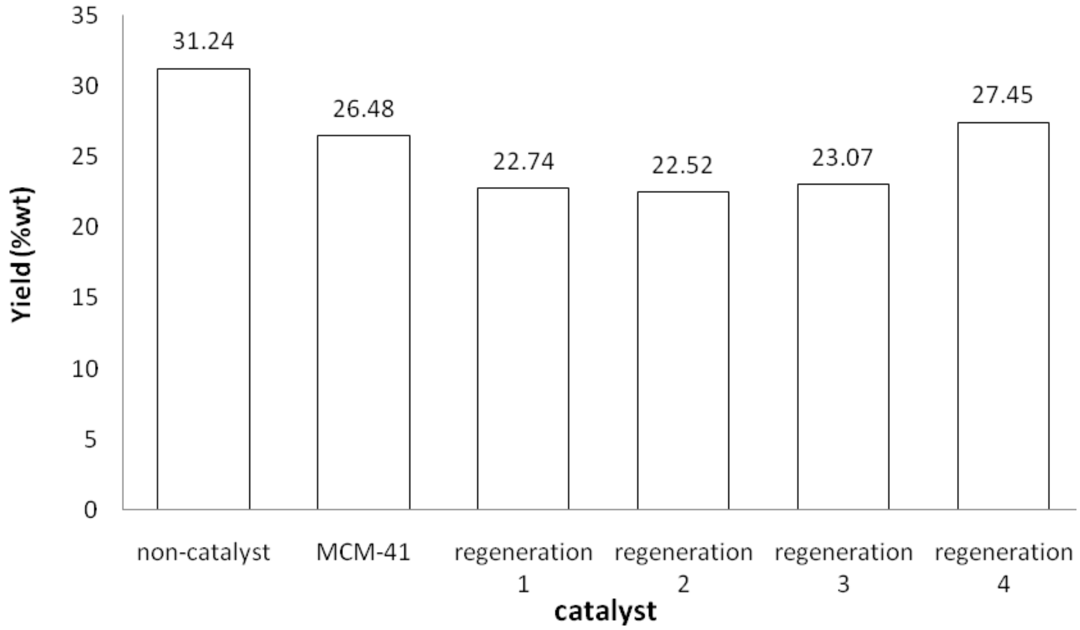

Figure 34 Polar fraction (%wt) of organic phase of bio-oils upgraded by fresh and regenerated MCM-41 at 673K

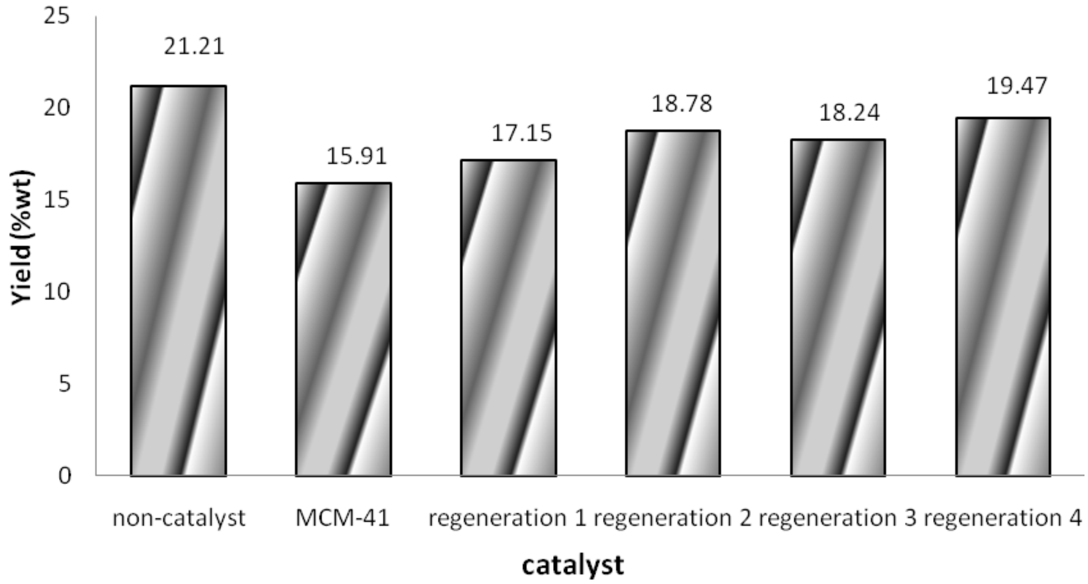

Figure 35 Asphaltene fraction (%wt) of organic phase of bio-oils upgraded by fresh and regenerated MCM-41 at 673K

Total energy output has the same trend as that of high heating value by decreasing of high heating value from the use of the third and fourth regenerated MCM-41(Figure 36). For aqueous phase, total energy output increased when MCM-41 was regenerated more than once (Figure 37).

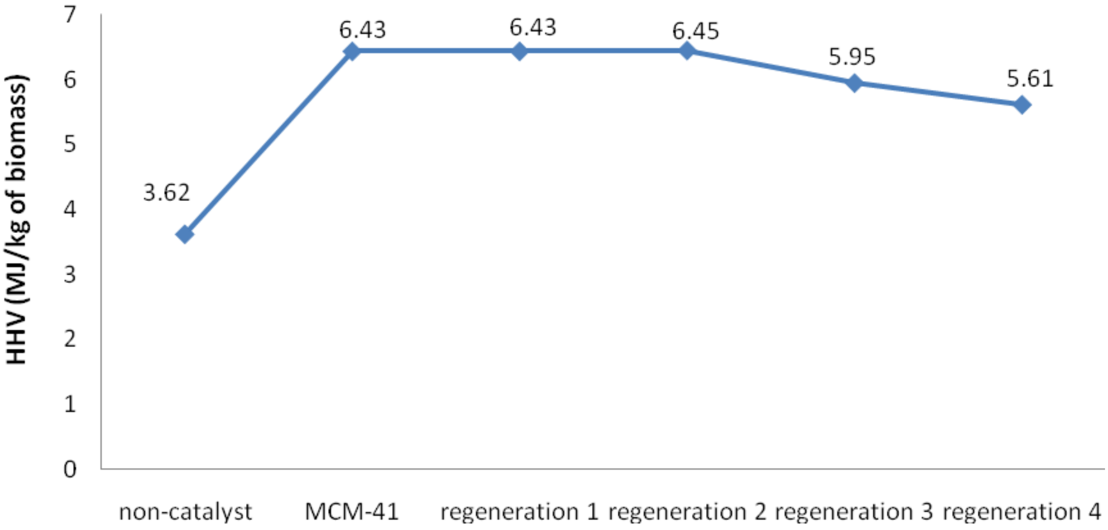

Figure 36 Total energy output (MJ/kg of biomass) of organic phase of bio-oils upgraded by fresh and regenerated MCM-41 at 673K

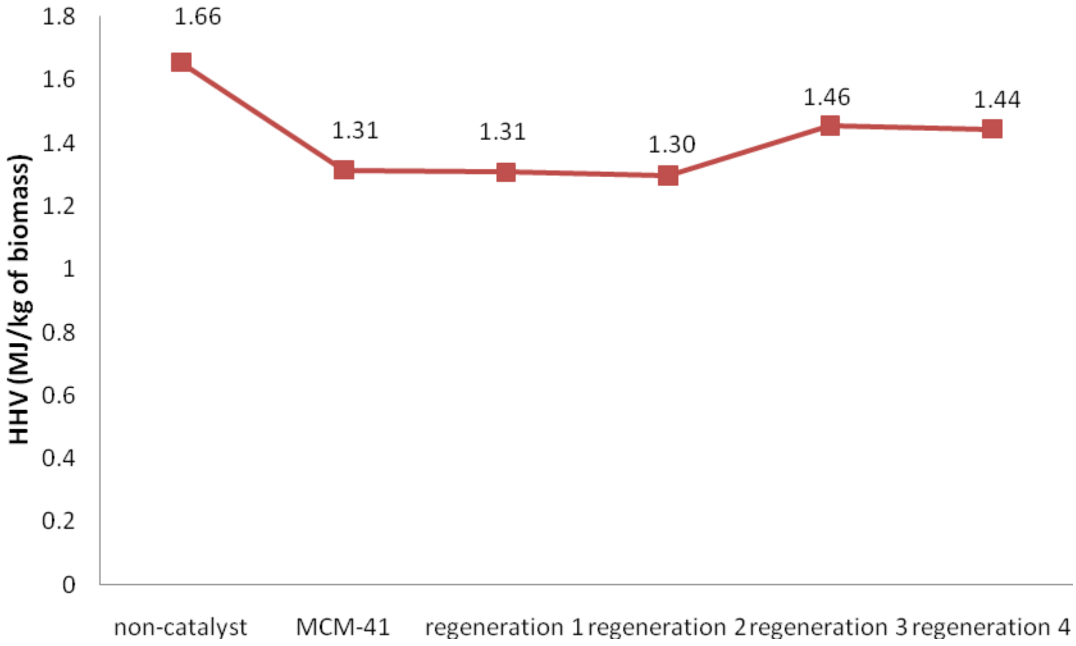

Figure 37 Total energy output (MJ/kg of biomass) of aqueous phase of bio-oils upgraded by fresh and regenerated MCM-41 at 673K

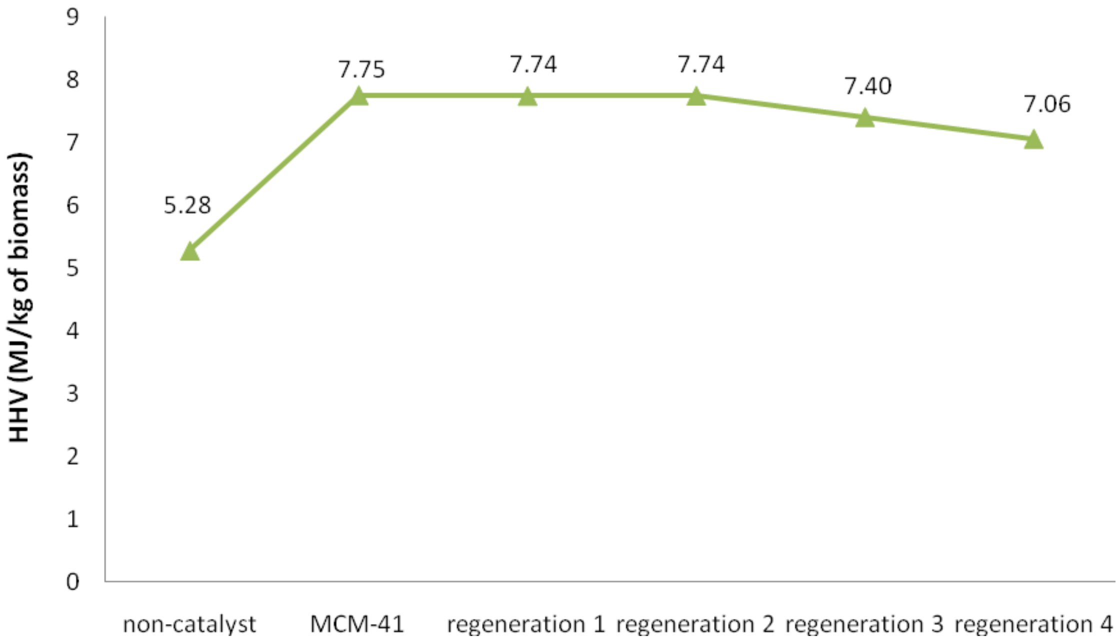

Figure 38 Total energy output (MJ/kg of biomass) of bio-oils (both organic and aqueous phase) upgraded by fresh and regenerated MCM-41 at 673K

HZSM-5 regeneration

The liquid yield (%wt) slightly decreased for regenerated HZSM-5 compared with fresh HZSM-5 and also the decrease of organic phase (table 8). In term of high heating value, all the regenerated HZSM-5 did not have significant effect on high heating value in both phases (35.8-36.5MJ/kg of regenerated HZSM-5 compared with 36.8MJ/kg of fresh HZSM-5 for organic phase and 4.5-4.7MJ/kg of regenerated HZSM-41 compared with 5.5MJ/kg of fresh HZSM-5 for aqueous phase) (Figures 39 and 40).

Table 8 Yields (%wt) of liquid product and the fractions of organic and aqueous phases of bio-oils upgraded by fresh and regenerated HZSM-5 at 673K

Time of regeneration	Yield (% wt)	organic phase (% wt)	aques phase (% wt)
non-catalyst	48.07	37.85	62.15
HZSM-5	46.79	35.88	64.12
regeneration 1	46.51	35.91	64.09
regeneration 2	47.23	35.94	64.06
regeneration 3	45.95	35.03	64.97
regeneration 4	45.67	34.97	65.03

In term of chemical class composition, bio-oils upgraded by regenerated HZSM-5 has unstable property by the change of chemical composition. When HZSM-5 was regenerated more than once, aliphaltic fraction decreased (Figure 41), aromatic fraction increased (7.98%wt of fresh catalyst compared with 20.3-21.8%wt of regenerated HZSM-5) (Figure 42), polar fraction decreased (Figure 43) and asphaltene fraction decreased for first and second regeneration and increased for third and fourth regeneration (Figure 44).

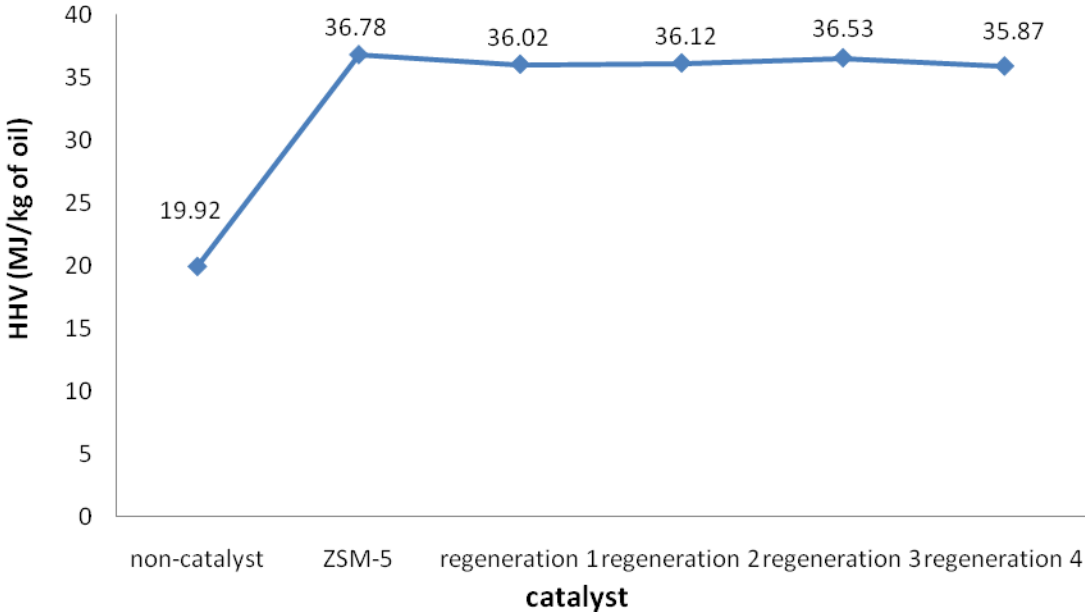

Figure 39 High heating values (HHV) (MJ/kg) of organic phase of bio-oils upgraded by fresh and regenerated HZSM-5 at 673K

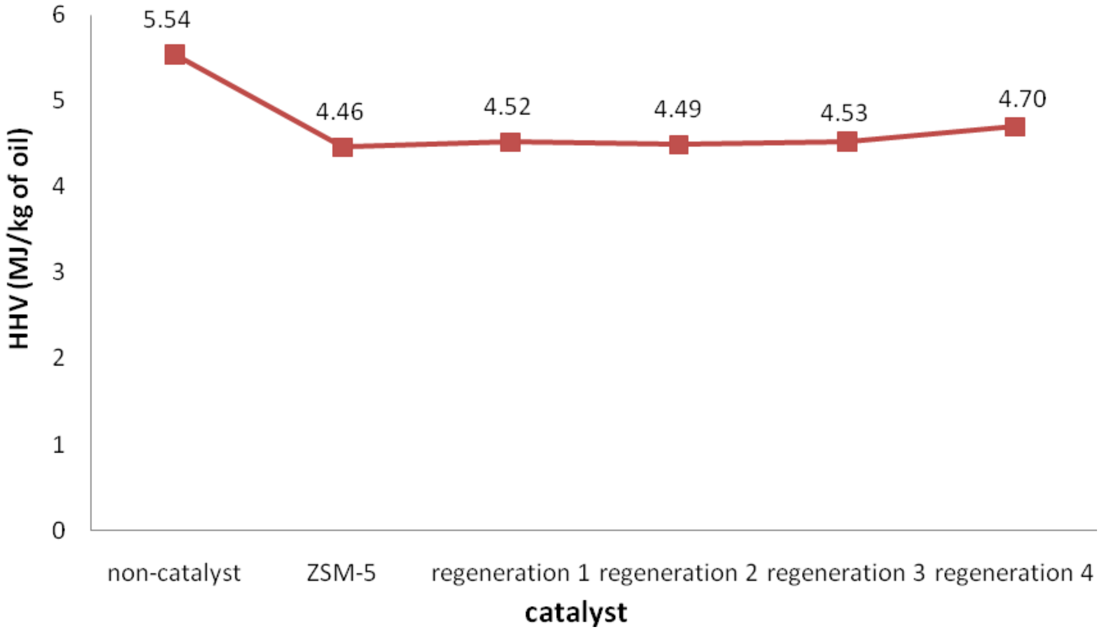

Figure 40 High heating values (HHV) (MJ/kg) of aqueous phase of bio-oils upgraded by fresh and regenerated HZSM-5 at 673K

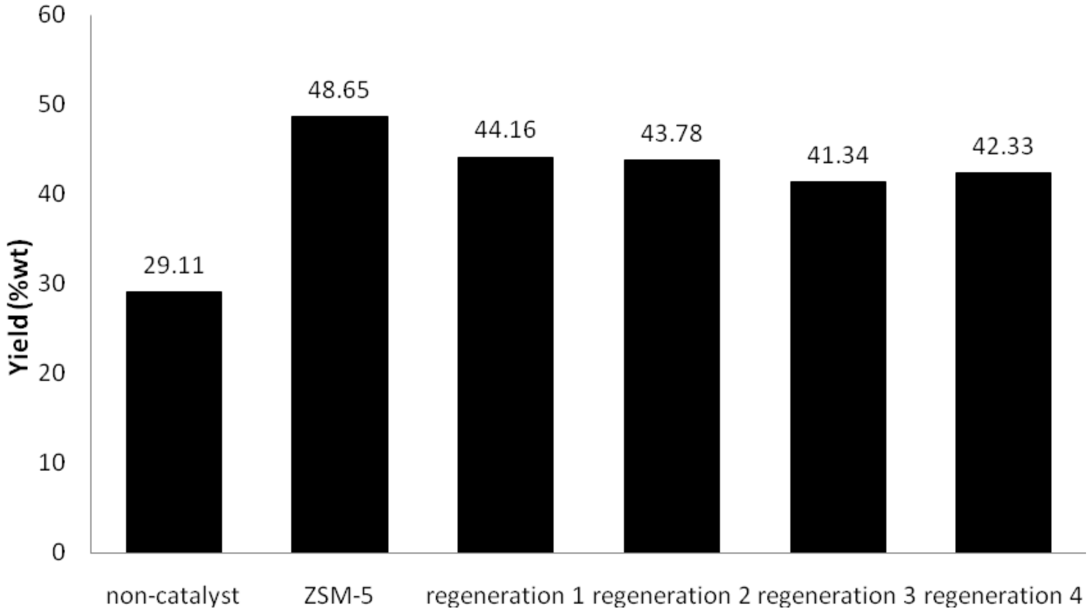

Figure 41 Aliphatic fractions (%wt) of organic phases of bio-oils upgraded by fresh and regenerated HZSM-5 at 673K

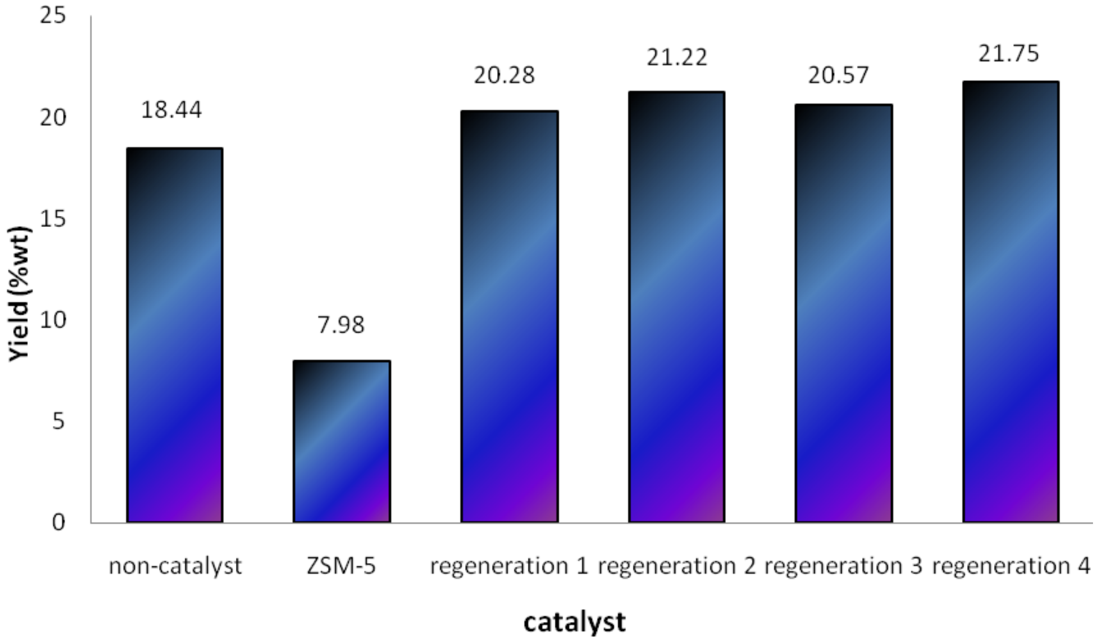

Figure 42 Aromatic fractions (%wt) of organic phases of bio-oils upgraded by fresh and regenerated HZSM-5 at 673K

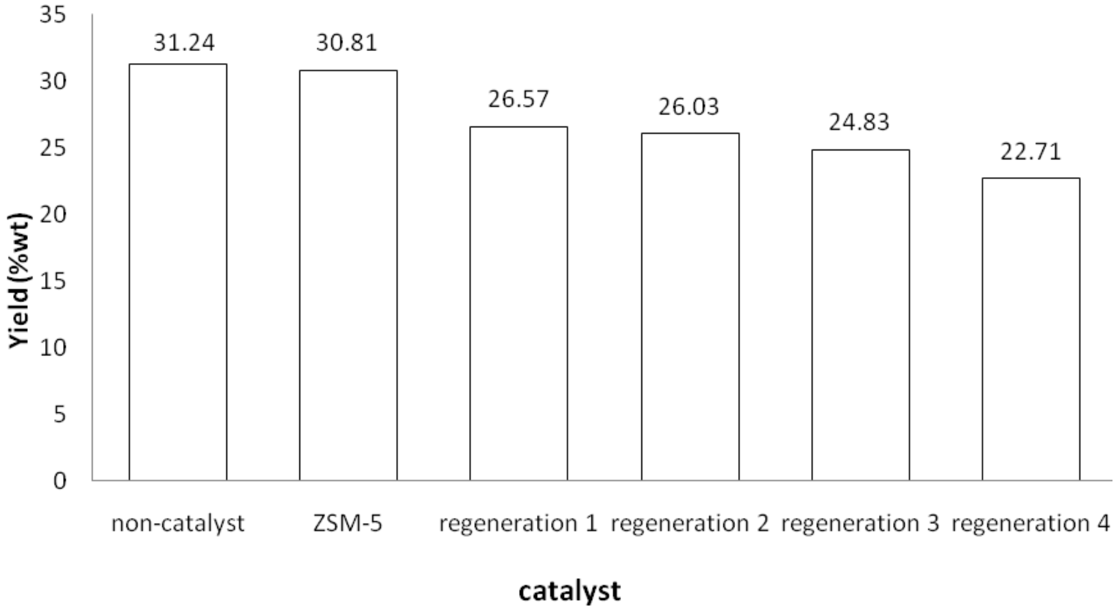

Figure 43 Polar fractions (%wt) of organic phases of bio-oils upgraded by fresh and regenerated HZSM-5 at 673K

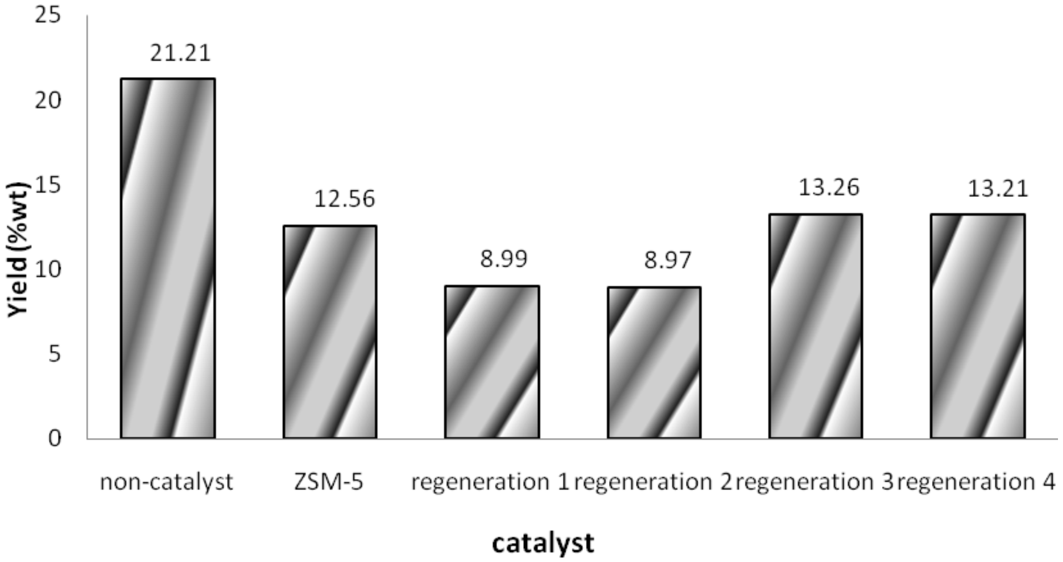

Figure 44 Asphaltene fractions (%wt) of organic phases of bio-oils upgraded by fresh and regenerated HZSM-5 at 673K

Even though high heating value of bio-oil upgraded by regenerated HZSM-5 did not change from that of fresh HZSM-5, total energy output in organic phase of bio-oil upgraded by regenerated HZSM-5 slightly decreased (5.7-6.1MJ/kg of biomass for regenerated HZSM-5 compared with 6.2MJ/kg of biomass for fresh HZSM-5). For aqueous phase, total energy output increased when HZSM-5 was regenerated more than once (Figures 45 and 46).

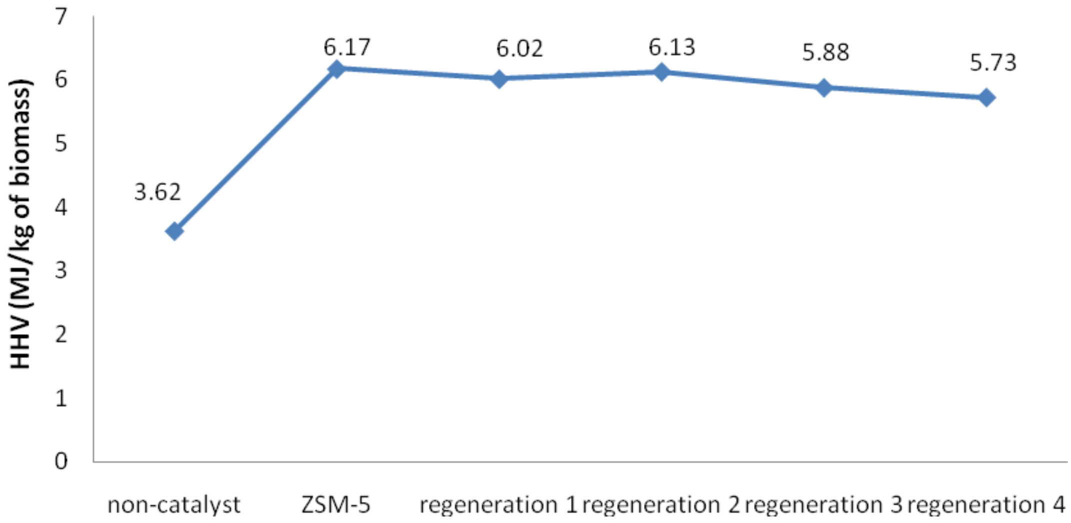

Figure 45 Total energy output (MJ/kg of biomass) of organic phase of bio-oils upgraded by fresh and regenerated HZSM-5 at 673K

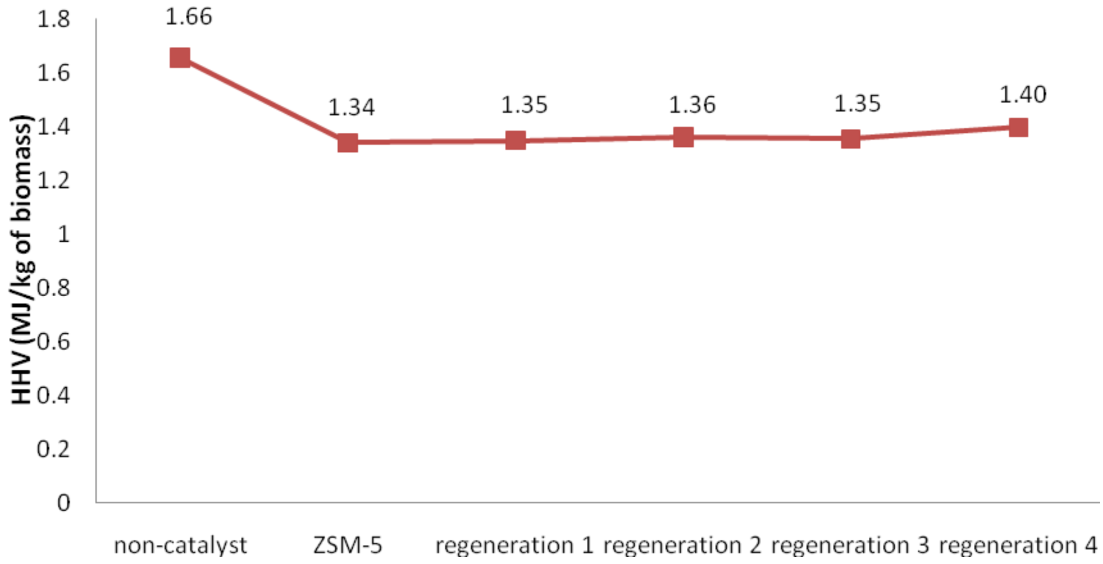

Figure 46 Total energy output (MJ/kg of biomass) of aqueous phase of bio-oils upgraded by fresh and regenerated HZSM-5 at 673K

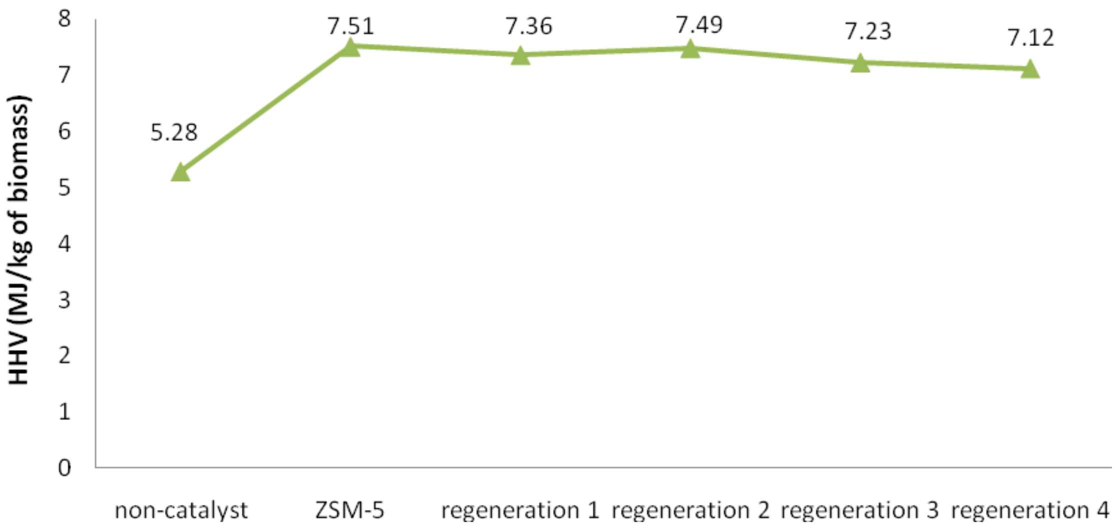

Figure 47 Total energy output (MJ/kg of biomass) of bio-oils (both of organic and aqueous phase) upgraded by fresh and regenerated HZSM-5 at 673K

The results of regeneration of both catalysts shows that MCM-41 can be regenerated twice only due to the reduction of its activity by decreasing of high heating value and the changing of chemical class composition. The results agree with those of Hyung *et al*. (2008). In their work MCM-41 had low thermal stability due to the hexagonal framework structures of Al-MCM-41 were significantly destroyed after it was regenerated considered by XRD. HZSM-5 can be regenerated for over four times without significant changes in terms of high heating value and total energy output from pyrolysis but in term of chemical class composition, bio-oil upgraded by the regenerated HZSM-5 shows the changes of their properties. The chemical class compositions changed due to the deactivation of acid site especially strong acid site (Vitolo *et al*., 2001). The results agree with Sinfrônio *et al.* (2006) research that HZSM-5 has higher thermal stability than MCM-41.

Conclusions and Recommendation

This experiment focuses on upgrading of bio-oil by MCM-41 and HZSM-5 and the synergistic effect of both catalysts. Both MCM-41 and HZSM-5 were packed with different MCM-41: HZSM-5 weight ratios of 1:1, 1:2 and 2:1 to investigate the effect of blending of the microporous and mesoporous materials. Pyrolysis of soybean cake took place in a fixed bed reactor at 673K in the absence of air and upgrading was in a packed bed tube reactor. The effect of sequence of catalysts packing and the effect of upgrading temperature were investigated.

The highest high heating value of the organic phase of bio-oil was by MCM-41 at 673 K which is 38.5 MJ/kg. Moreover, aliphatic compounds increased from 29 to 47%wt and asphaltene compound decreased from 21%wt to 16%wt. MCM-41 shows the best performance due to its pore size which does not limit molecule size of liquid product like HZSM-5 and diffusion limit like MMZ. Blending of catalyst did not improve its property, considering from the high heating value and the sequence of catalysts packing. Hybrid catalyst MMZ, HZSM-5 and MCM-41 increased aliphatic and decreased other fractions. The chemical composition of MMZ is similar to that of the blend of MCM-41 and HZSM-5 with the ratio of 1:2. For the effect of temperature, the optimum upgrading temperature is 673K. HZSM-5 can be regenerated at least four times while MCM-41 can be regenerated only two times without significant changes of high heating value and total energy output from pyrolysis but in terms of chemical class composition. It could be concluded that MCM-41 shows the best performance among HZSM-5 and MMZ.

The coke decomposition of catalysts could be further analyzed by ammonium temperature programmed desorption (NH_3-TPD) to study thermal stability of catalysts especially MCM-41.

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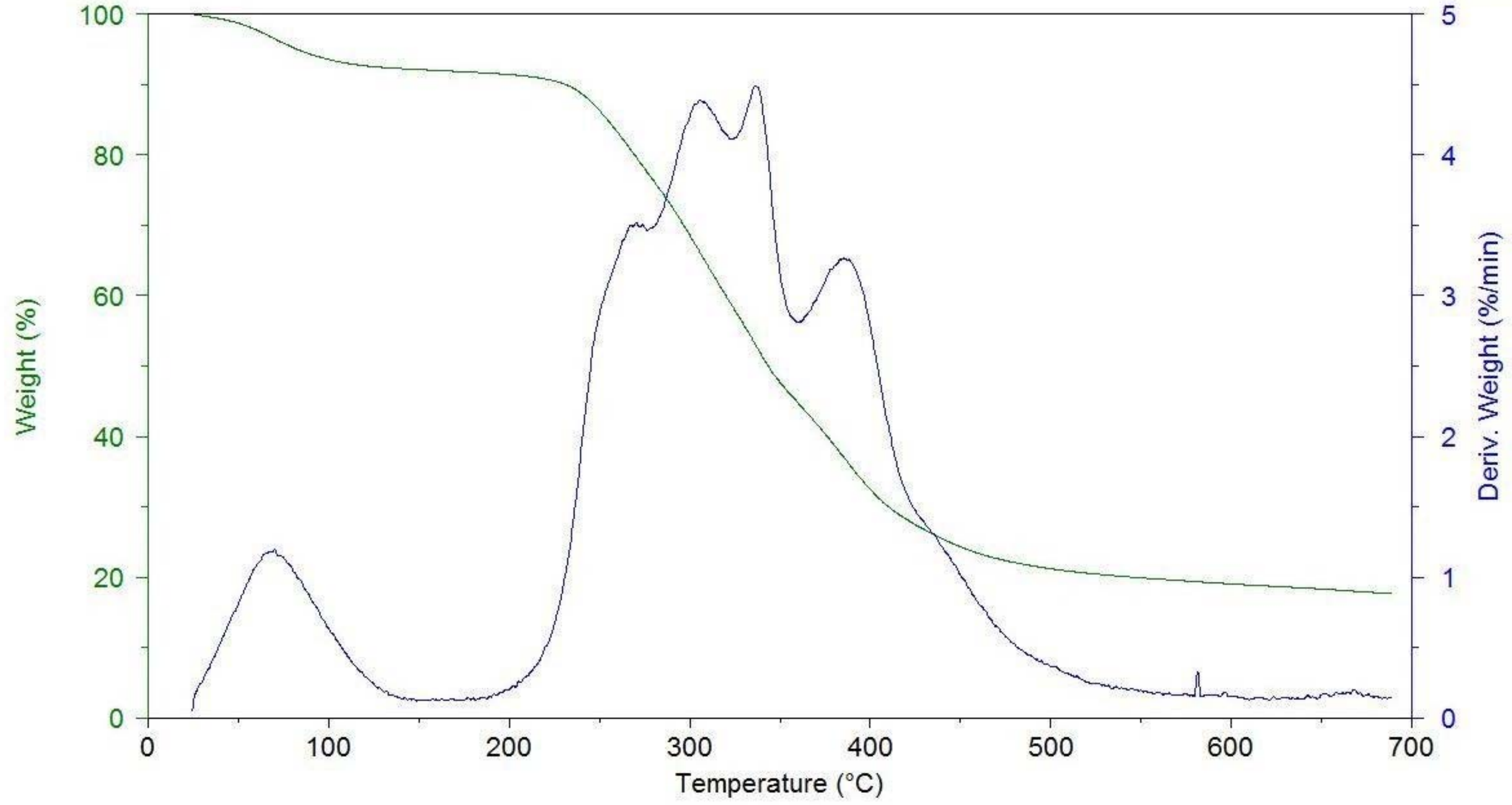
APPENDICES

Appendix A

TGA-DTG of soybean cake



Appendix Figure A1 TGA-DTG curve of soybean cake

Appendix B

Product yield from non-catalyst and upgrading reaction

Appendix Table B1 Product weight (g) of bio-oil, char and gas from upgrading and non-catalyst reaction at 673K

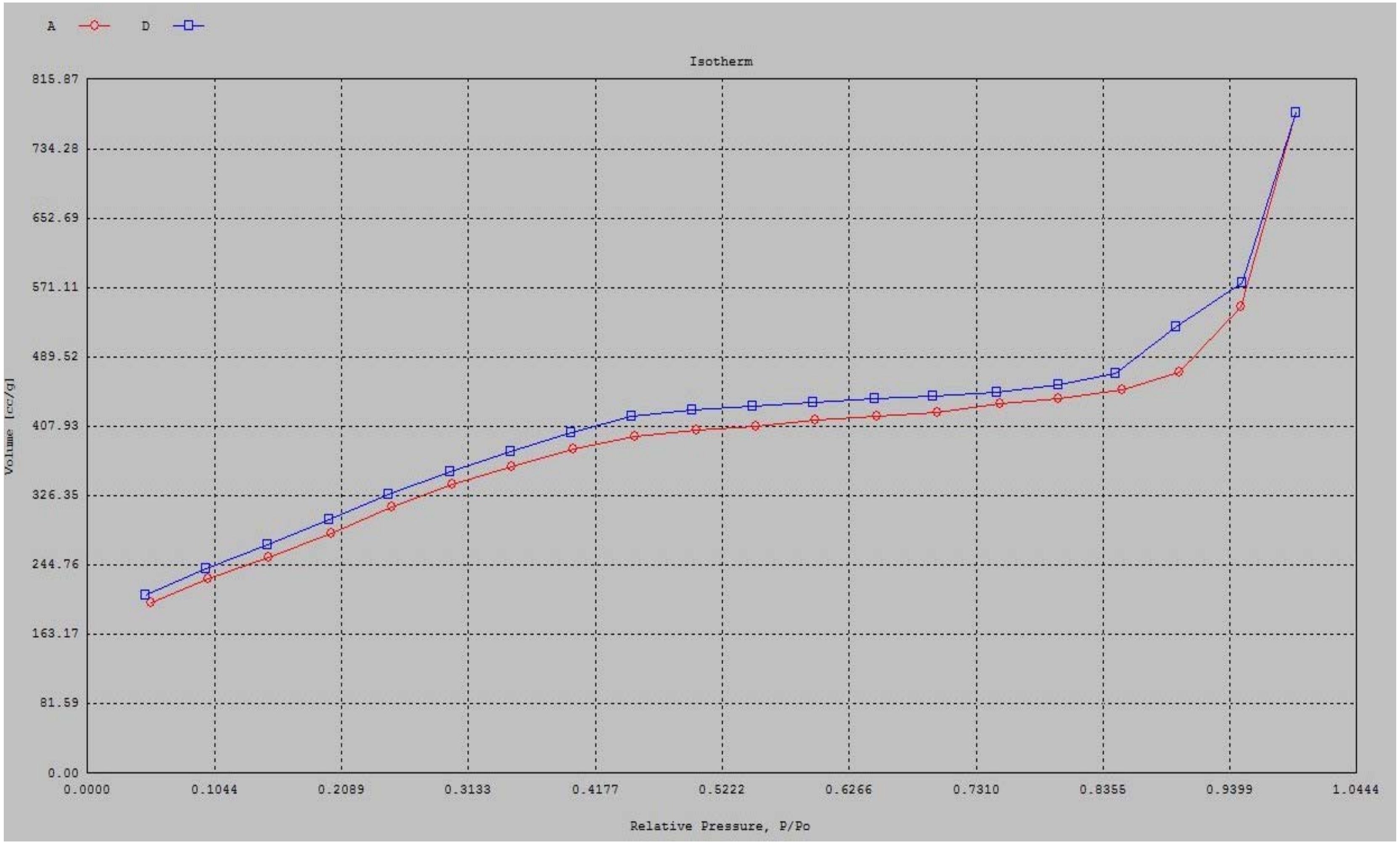
Type of upgrading reaction	Bio-oil (g)	Char (g)	Gas (g)
non-catalyst reaction	120.18	58.98	71.03
upgrading by MCM-41	120.05	59.25	70.70
upgrading by HZSM-5	116.98	59.00	74.03
upgrading by mixed catalysts MCM-41: HZSM-5 = 2: 1 (by weight)	119.33	59.08	71.60
upgrading by mixed catalysts MCM-41: HZSM-5 = 1: 1 (by weight)	115.90	60.03	74.03
upgrading by mixed catalysts MCM-41: HZSM-5 = 1: 2 (by weight)	118.50	59.18	72.33

Appendix Table B2 Weight (g) of organic phase and aqueous phase in bio-oil from upgrading and non-catalyst reaction at 673K

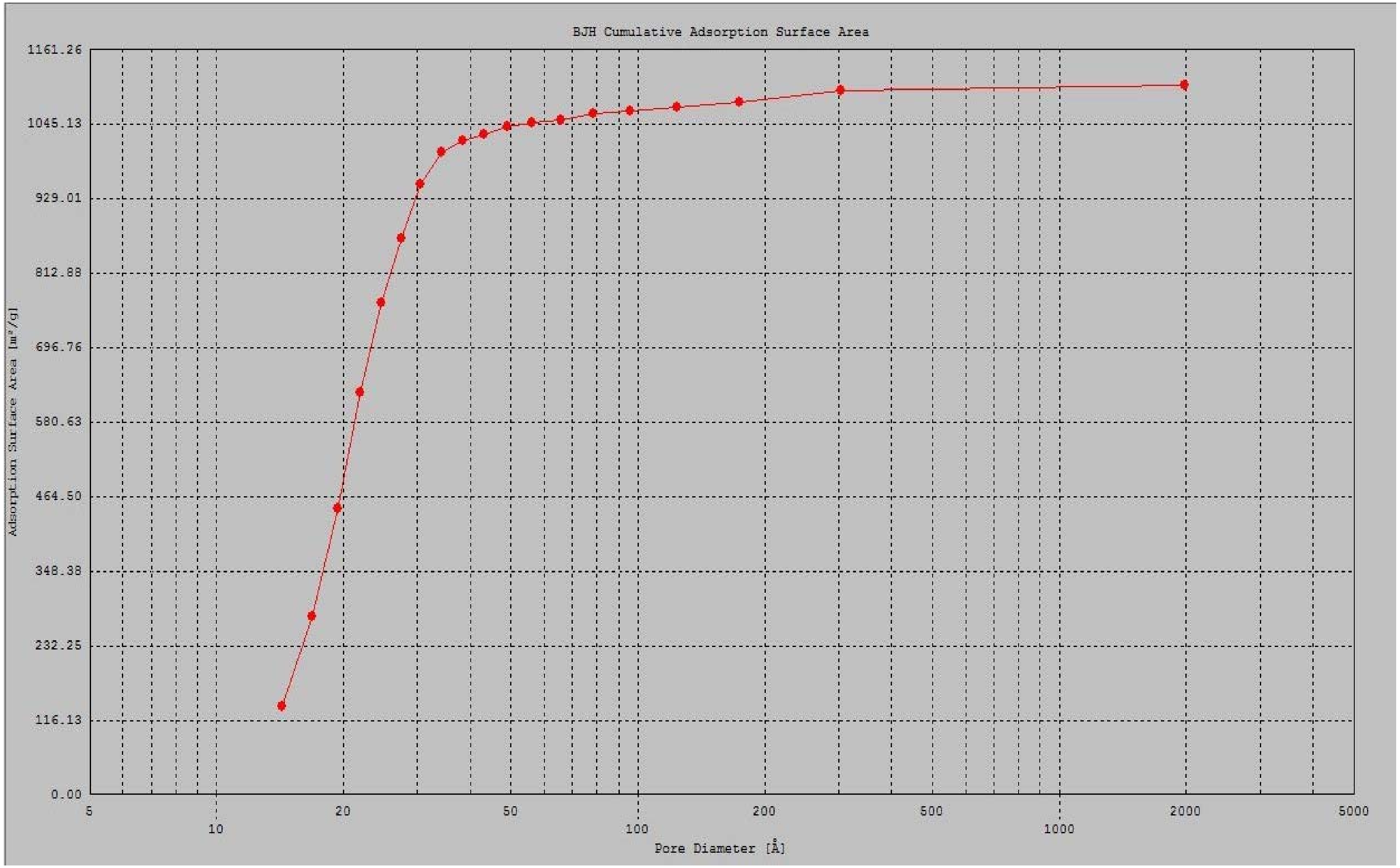
Type of upgrading reaction	bio-oil (g)	Organic phase (g)	Aqueous phase (g)
non-catalyst reaction	120.18	45.49	74.69
upgrading by MCM-41	120.05	41.83	78.22
upgrading by HZSM-5	116.98	41.97	75.00
upgrading by mixed catalysts MCM-41: HZSM-5 = 2: 1 (by weight)	119.33	42.41	76.92
upgrading by mixed catalysts MCM-41: HZSM-5 = 1: 1 (by weight)	115.90	38.25	77.66
upgrading by mixed catalysts MCM-41: HZSM-5 = 1: 2 (by weight)	118.50	39.26	79.24

Appendix C

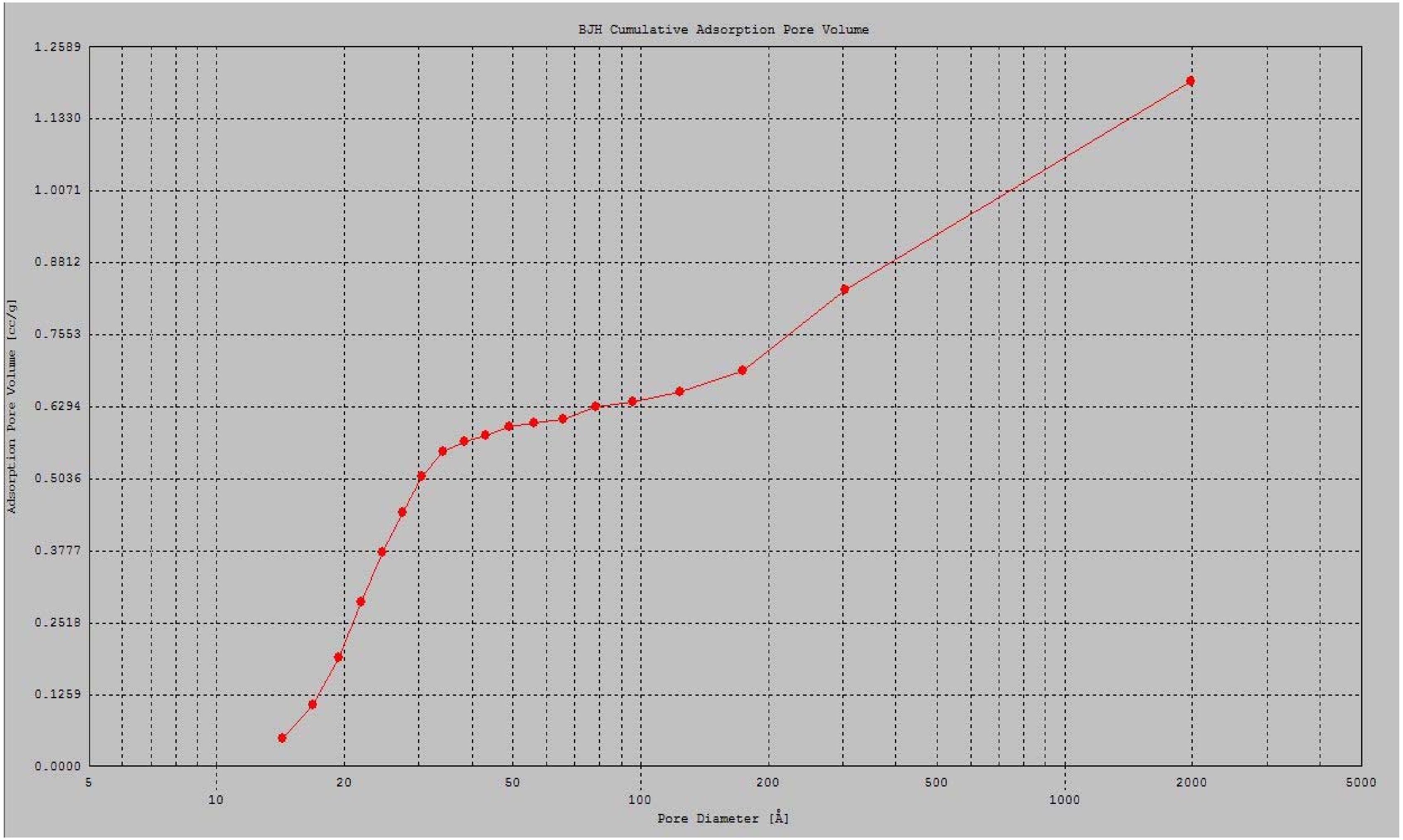
Characterization of MCM-41



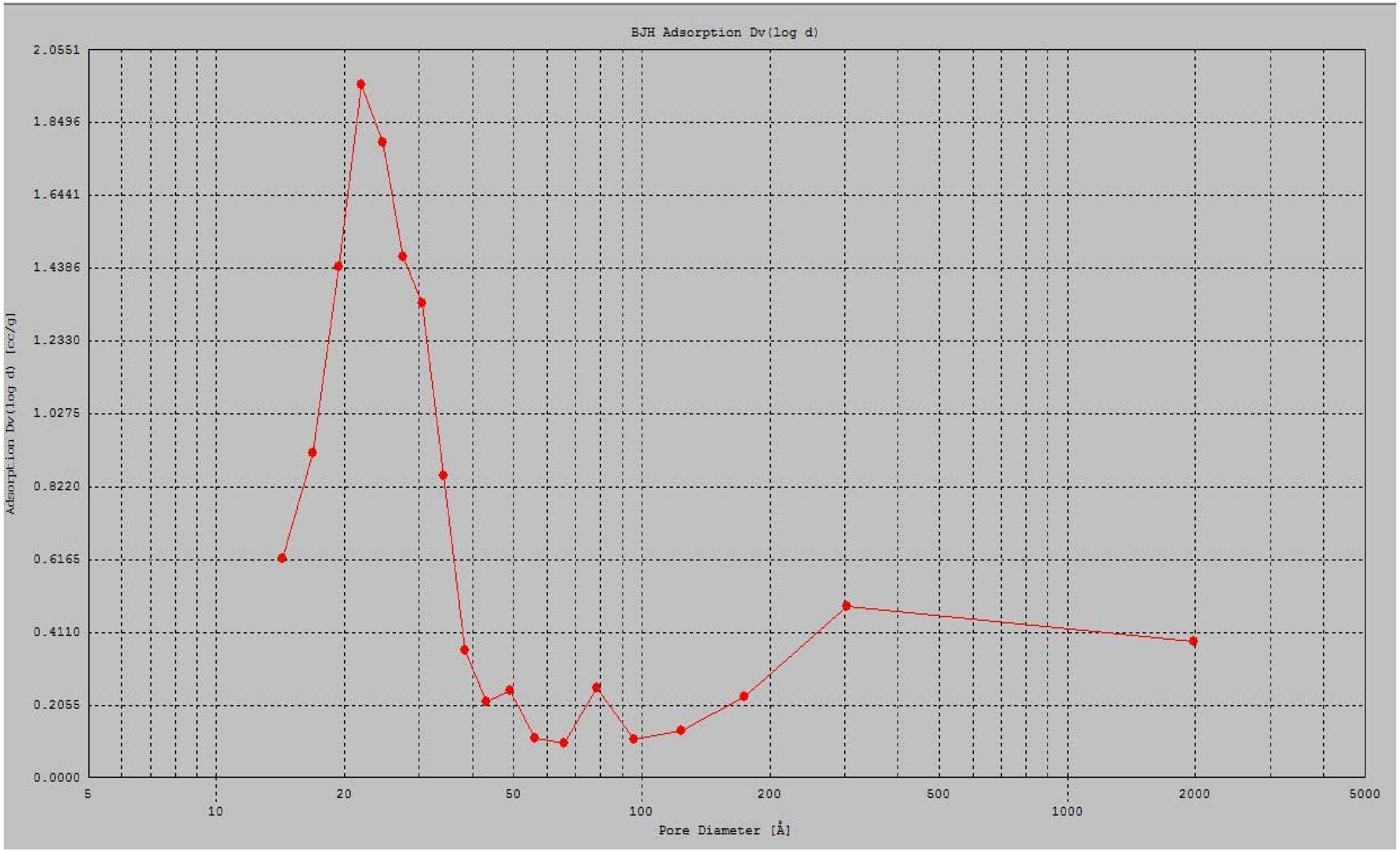
Appendix Figure C1 Adsorption and desorption isotherm of MCM-41



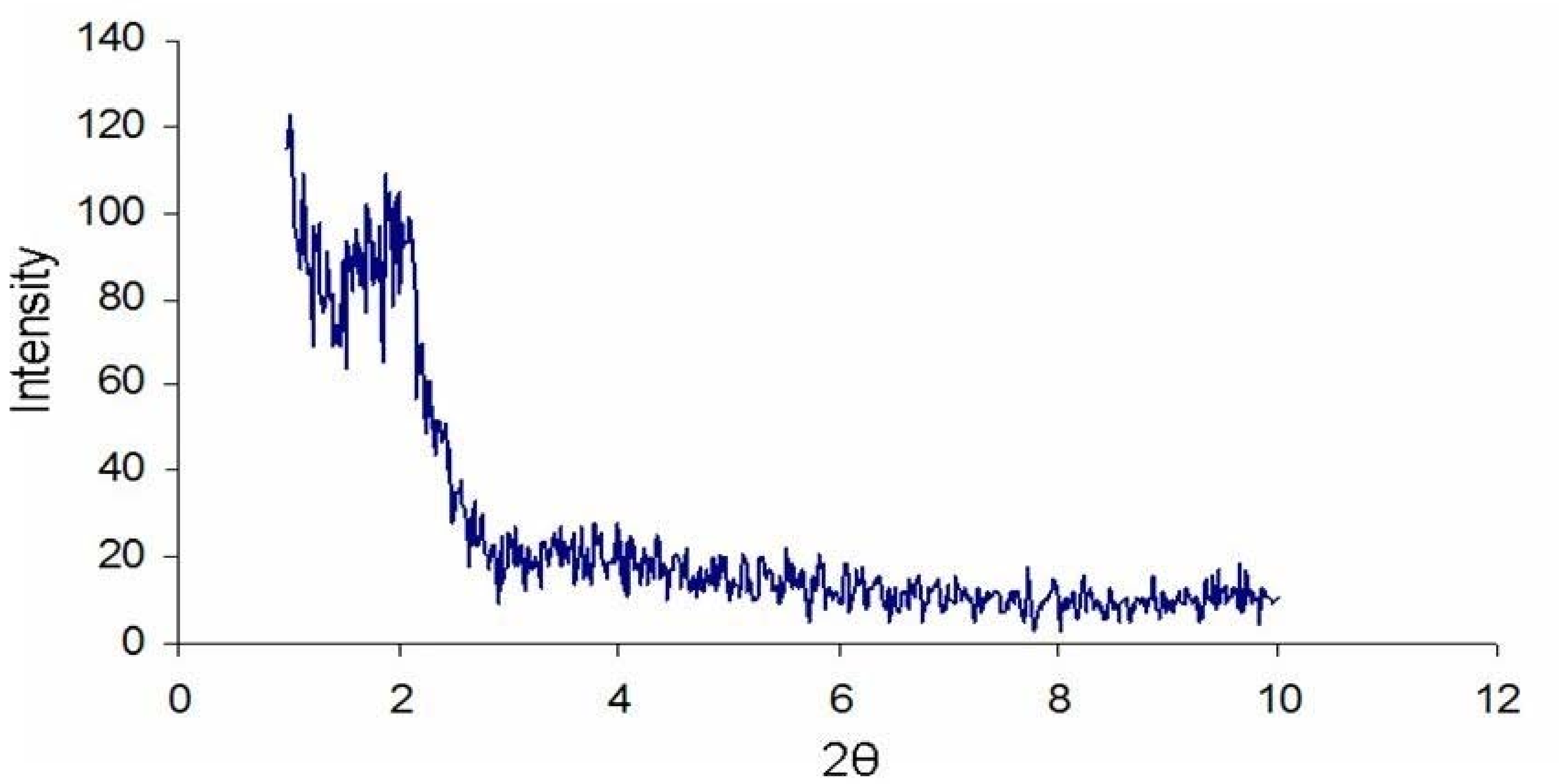
Appendix Figure C2 Surface area of MCM-41



Appendix Figure C3 Adsorption pore volume of MCM-41



Appendix Figure C4 Pore size distribution of MCM-41



Appendix Figure C5 XRD pattern of the MCM-41

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