Bio-Oil Upgrading by Catalytic Cracking Over Different Solid Catalysts

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Abstract: Fossil fuel crises along with global environmental issues, due to combustion of fossil fuel, lead to focus on biomass derived fuels. Bio-oil nowadays is seriously considered to be one of the favorable, renewable and alternative energy sources to replace fossil fuel and has become a significant energy carrier for transportation, industrial and commercial applications. In this study, bio-oil was upgraded by catalytic cracking in a fixed bed reactor in the presence of three different catalysts HY, H-mordenite and HZSM-5.All of the experimental runs were carried out at 500 °C, 0.3MPa and 15:1 oil to catalyst ratio. Catalysts characterization revealed that HZSM-5 with uniform pore and TPD analysis shows the presence of large number of acidic sites as compared to HY and H-mordenite. HZSM-5 proved its effectiveness in terms of deoxygenation and converting oxygenating compounds to hydrocarbons. The amount of hydrocarbons formed was 16.27 wt % OLP for HZSM-5, 15.16 wt% for HY and 14.954 wt % for H-mordenite. HZSM-5 possessed a strong acidity, uniform pore size and high activities which tended to permit the transformation of the oxygenated compounds present in the bio-oil to hydrocarbons. The upgraded bio-oil obtained posses improved physiochemical properties such pH which was increased from 2.21 to 3.56 while density was decreased upto 0.82 kg/m^3. The calorific value also increased upto 31.65 kJ/kg. The improved bio-oil by HZSM-5 catalyst can be considered as a potential for to be used as direct fuel.

Keywords: Bio-oil, Upgrading, HZSM-5, Characterization, Catalytic cracking, Deoxygenation.

1. INTRODUCTION

Due to the continuous increase in population and industrialization, energy consumption is increasing but energy sources are decreasing [1, 2]. Most of the developing countries are facing two major problems related to fossil fuel such as emissions and the limited resources [3]. Due to the burning of fossil fuels SOx and NOx are emitted which are the major cause of acid rain and greenhouse gas that posed major threat to world climate [4, 5]. If this phenomenon continues, it is forecasted that some extreme natural calamities are expected.

Biomass is being considered to be an efficient alternative energy resource via convert to liquid product in high heating process named as pyrolysis [6]. Vapors produced by pyrolysis of biomass are condensed to a liquid product known as bio-oil that has dark brown color and pungent smell [7]. Bio-oil or pyrolysis oil has the potential to be an alternative to fossil fuel. Crude bio-oil can be used directly in boilers, different important chemicals can be separated from it and it can also be upgraded so that it can be used in engines for energy generation. Bio-oil contains large amount of oxygen almost 35-40 wt% [8] and can be decomposed to release oxygen as H2O, CO_2 or CO in the presence of catalyst to form hydrocarbon [9].

Bio-oil has potential as an alternative fuel to replace fossil fuel. Contrast to fossil fuel, bio-oil is considered to be CO_2 neutral [10] and contains very minor quantity of nitrogen and sulfur. Consequently, bio-oil usage contributes less air pollutants and greenhouse gases into the environment [11]. However there are some limiting properties that restrict bio-oil to be used at large scale such as high oxygen and water contents, high viscosity and low calorific value [12].

The direct usage of bio-oil as substitute for conventional petroleum fuels is therefore limited and consequently, upgrading of bio-oil has attained the great interest [9]. Upgrading process for bio-oil mainly involves the removal of oxygenated compounds or their conversion into light hydrocarbons with high calorific value [13]. Mostly, two methods has been proposed for

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upgrading *i.e*. catalytic hydrotreatment in presence of hydrogen [14-16] and catalytic cracking [17-19] that does not require hydrogen. Catalytic cracking in the absence of hydrogen for upgrading of bio-oil has gained the great interest and many researchers have worked on this [10, 18, 20, 21] due to its cost competitiveness.

The selection of catalyst plays important role in catalytic cracking, and zeolite based catalyst is thought to be most effective for cracking process [10, 22, 23]. The nature of the product obtained after catalytic cracking depends upon the type of catalyst: when HZSM-5 is used aromatic hydrocarbons are obtained, while aliphatic hydrocarbons are obtained when HY-Zeolites based catalyst are used for upgrading [10]. Acidic sites in HZSM-5 lies on the intercrystaline surface and all are easily accessible for cracking. Molecules ranging from $C_6 – C_{10}$ can easily diffuse due which HZSM-5 is considered to be beneficial for cracking and aromatization of heavy hydrocarbons [13]. H-Mordenite and HY are large pore zeolites and possess both Lewis and Bronsted acidic sites. H-Mordenite has channel like pore structure in which basic building block consist of five membered rings. Diffusion in H-Mordenite pore structure is in parallel channels. So HY and H-Mordenite allows larger hydrocarbons feasibility for cracking [24]. In catalytic cracking, the hydrocarbon yield was thought to be less due to high coke and char formations and deactivation of catalyst [24].

In this work, catalytic cracking of bio-oil over HY, H-mordenite and HZSM-5 catalysts in a continuous fixed bed reactor was investigated. As bio-oil contain number of chemical compounds with complex nature, it becomes difficult to estimate the conversions. To overcome the complications and to ensure consistencies in the study, the model compounds majorly present in bio-oil *i.e*. phenol, ketones, acetic acid, aldehyde and water were used to study the cracking performance. Degree of de-oxygenation wasalso calculated at different operating temperatures.

2. MATERIALS AND METHODS

2.1. Bio-oil

Model bio-oil samples were freshly prepared before each experiment which consisted of acetic acid (10 wt %), 2-furaldehyde (20 wt %), acetone (10 wt %), phenol (30 wt %) and water (30 wt %).

2.2. Catalyst

Three different types of catalysts have been used in this work Table (**1**). HZSM-5 and HY catalyst has similar SiO_2/Al_2O_3 ratio 30:1 while for H-mordenite it was 20:1. The surface area of HZSM-5 is the lowest among all with 400 m^2/g while for HY and H-Mordenite it is 680 and 500 m^2/g, respectively.

Table 1: Catalyst Characterizations

Catalyst	SiO_2/Al_2O_3	Surface Area(m^2/g)
HZSM-5	30:1	400
HY	30:1	680
H-Mordenite	20:1	500

2.3. Catalyst Characteristics

Scanning electron microscopy Oxford LEO 1430 was used for obtaining the surface morphology. Surface images for all samples were taken at a magnification of 20 KX. The Thermo Scientific TPDRO 1100 with TCD detector was used for ammonia temperature programmed desorption (NH_3-TPD) measurements. About 100 mg of sample was placed in a U-shaped quart tube with ID = 4mm. The sample was first pretreated at 300ºC for 2 hr in a He- stream at 100 ml/min. After being cooled down to 20ºC, the pretreated sample was exposed to NH_3 for 30 min. After that, the sample was purged with a He air stream at 20ºC until the baseline of NH_3 in the mass spectrum was steady. Finally, the NH_3-TPD was performed at the rate of 10ºC/min in a He flow from 30ºC to the required temperature.

Bruker-AXS D8 Advance was used for the X-ray diffraction (XRD) patterns. The pore size and surface area were calculated based on the Brunauer-Emmett-Taylor (BET) method while the pore volume was calculated based on the Barrett-Joyner-Halenda (BJH) method. The Physisorptionanalyser Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry was used for obtaining the N_2 adsorption-desorption isotherms. A sample weighing 0.1444±0.0001 g was first degassed at 300 ºC for 4 hrs. Then, the analysis was carried out based on the measured content of liquid N_2 adsorbed and desorbed at its boiling conditions (-196 ºC and 1atm). The total gas quantity adsorbed or desorbed was recorded at the standard temperature and pressure (0 ºC and 1atm) conditions.

2.4. Fixed Bed Reactor

All the experiments were conducted in fixed bed reactor as shown in Figure (**1**). Initially, the reactor was loaded with 3 g of catalyst on glass wool supported by wired fixed bed and the upper surface of the catalyst was again covered by glass wool. The reactor was therefore placed in a furnace. The reactor was heated to desired temperature and purged continuously with N_2 gas (50 ml/min) until desired temperature and pressure conditions were achieved. Subsequently, the bio-oil was pumped into the reactor with constant flow rate of 1 ml/min. Finally, the condensed liquid products were collected at the outlet of the condenser while gaseous products were collected in gas tank. Thereafter, both collected products were subjected to GC analysis.

Two performance indicators calculated that include are oil yield and degree of de-oxygenation:

$$Y_{oil} = \left(\frac{m_{oil}}{m_{feed}} \right) \times 100\% \qquad (1)$$

$$DOD = \left(1 - \frac{O_2 wt\%_{inproduct}}{O_2 wt\%_{\inf eed}} \right) \times 100\% \qquad (2)$$

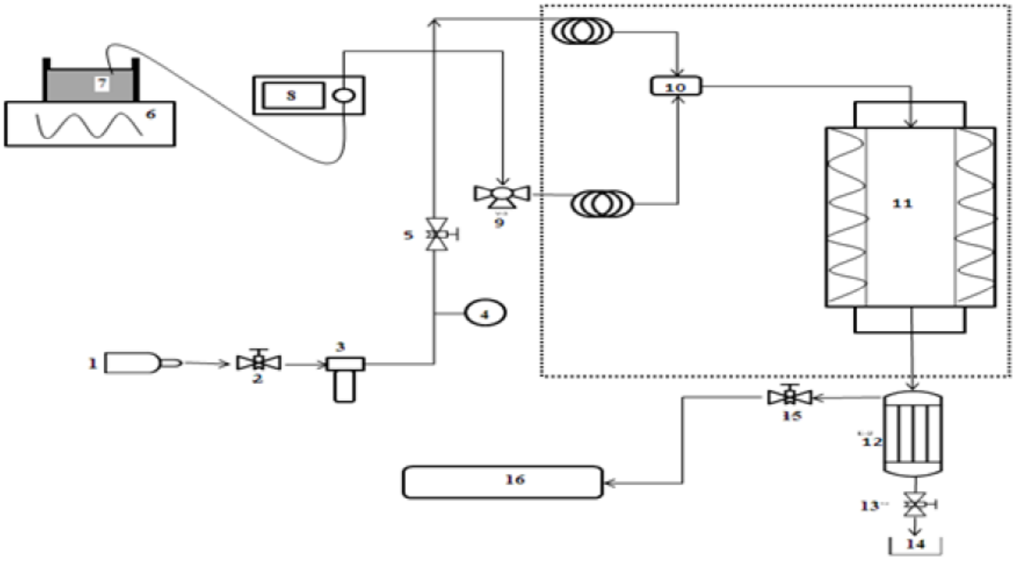
Where: Y_{oil} is the yield of oil, m_{oil} is the weight of produced oil, m_{feed} is the weight of feed, DOD is the degree of de-oxygenation and *wt%* is weight percent of oxygen in oil. These two parameters give an overview of the extent of reaction.

3. RESULTS AND DISCUSSIONS

3.1. Catalyst Characterization

3.1.1. XRD Analysis

The XRD spectrum of the HZSM-5, HY and H-Mordenite is shown in Figure (**2**). The spectrum of the HZSM-5 catalyst showed the crystalline nature based on the presence of the main peaks at 7º to 10º and 23º to 25º on the scale of 2θ. The main peaks which indicated the crystalline nature of the commercial HZSM-5 were present within the ranges of 7º to 10º and 23º to 25º. The main peaks presented from 5º to 35º show a high crystallinity for the HY catalyst. It can be observed from Figure (**2**) that H-mordenite was crystalline in nature as major peaks which reflect this observation lie between 5º to 10º, 13º to 15º, 19º to 20º, 22º to 23º and 25º to 30º. A similar kind of observations has been reported by Sheng *et al*. [25].



1. N_2 gas Cylinder
2. Valve V1
3. Flow controller
4. Pressure Controller
5. Valve V2
6. Hot plate
7. Bio-oil
8. Syringe Pump
9. Valve V3
10. Preheater
11. Fixed Bed Reactor
12. Condenser
13. Valve V4
14. Liquid Product Collector
15. Valve V5
16. Gas Collector

Figure 1: Process flow diagram of catalytic cracking unit.

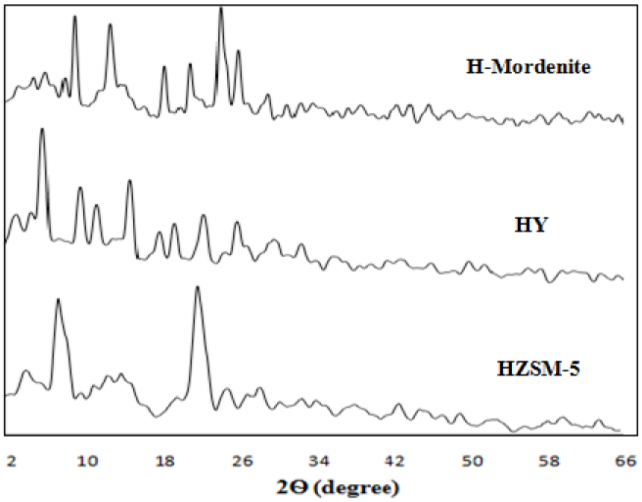


Figure 2: XRD patterns for HZSM-5, HY and H-Mordenite.

3.1.2. Scanning Electron Microscopy (SEM) Analysis

The SEM analysis was used to analyse the surface morphology of all three catalysts used in the present work. Figure (**3**) shows the surface image for the commercial HZSM-5, HY and H-Mordeniteat the 20.0 KX magnification. It can be observed that all of the particles in HZSM-5 were in the crystalline shape and the sizes of all particles were evenly distributed, but for HY it can be observed that based on the particle size, they were not evenly distributed and for H-Mordenitethe particles were in a pellet type shape while the particle size was also not uniform. It did not change with a large variation from particle to particle. All catalysts are porous in nature and can be used for cracking. But as it can be observed, HZSM-5 has uniform distribution of particles compared to HY and H-Mordenite, which gives HZSM-5 better cracking in term of higher DOD of product which causes high formation hydrocarbons. HY and H-Mordeniteparticles were scattered and also did not posses uniform pore volume due to which reactants are not properly converted. Similar observations have been reported by Adjaye [18].

3.1.3. Physisorption Analysis

The N_2Physisorption analysis was carried out to find out the pore volume and surface area, and to check the adsorption-desorption behaviour of HZSM-5, HY and H-Mordenite. The BET surface area of HZSM-5, HY and H-Mordenite which includes the pore volume, pore size and surface of the catalyst are shown in Table (**2**).

Table 2: Surface Properties of HZSM-5, HY and H-Mordenite

Parameters	HZSM-5	HY	H-Mordenite
Pore size (nm)	2.9	6.8	8.2
Pore volume (cm^3/g)	0.09	0.17	0.05
BET surface area (m^2/g)	330	710	465

3.1.4. TPD Analysis

Figure (**4**) shows the NH_3-TPD patterns for the three different catalysts. The area under each peak represents the amount of ammonia desorbed and the position represents the strength of the acidity. The NH_3 desorption curve for the HZSM-5 represented two peak patterns 200-300 ºC and 450-500 ºC which indicates the presence of weak acidic sites and strong acidic sites. The pattern of the NH_3 desorption was consistent with the literature already presented for the HZSM-5 catalyst [26]. Meanwhile, for H-Mordenite, the NH_3 desorption pattern shows that the intensity of the weak acidic sites was higher as compared to the strong

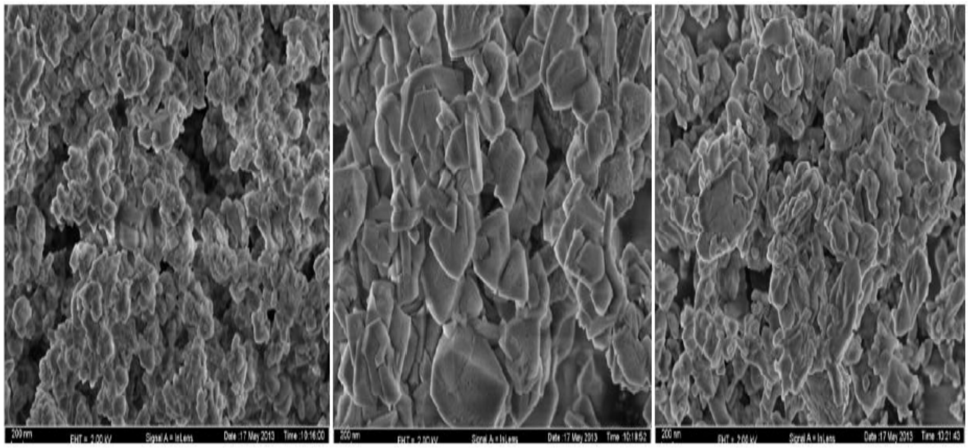


Figure 3: Surface Image of HZSM-5, HY and H-Mordenite.

acidic sites. Furthermore, for the HY zeolite catalyst, the peak for the weak acidic sites was quite significant but in terms of the strong acidic sites, they were not too obvious. Cui *et al*. [27] presented a similar kind of results for the Y-Type zeolite catalyst. Sombatchaisac *et al*. [28] reported that the strength of the strong acidic sites was less in the HY catalyst as compared to the weak acidic sites, and the trend indicated by them was in a similar way as for the present work.

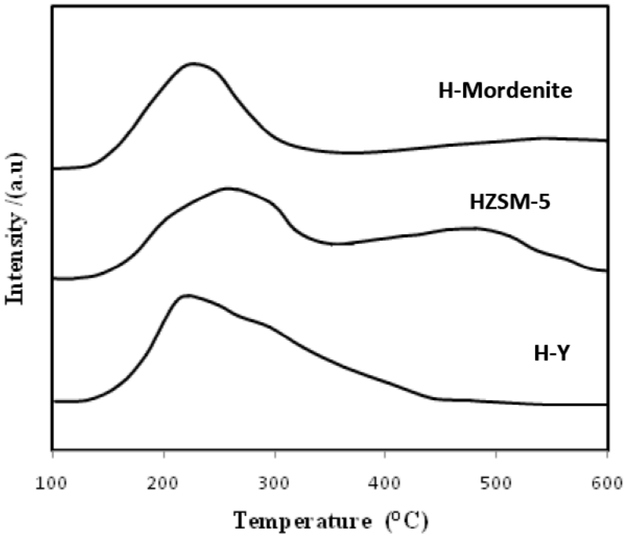


Figure 4: Ammonia TPD for HZSM-5, HY and H-Mordenitesamples.

3.2. Product Evaluation

In order to evaluate the performance of the catalyst and to prove the concept that HZSM-5 is the most appropriate catalyst for upgrading bio-oil by catalytic cracking, a comparison between the different catalysts was performed. Upgrading of the model bio-oil by catalytic cracking was carried out under optimized conditions (500 ºC, 0.3 MPa, and O/C ratio of 15:1) obtained from a parametric study for catalytic cracking of model bio-oil in the presence of HZSM-5 as discussed before. The overall product distribution for upgrading the model over three catalysts is shown in Table (**3**).Since deoxygenation was the major concern for the upgrading of bio-oil, it was important to measure the products concerned, such as gases which were mainly eliminated due to decarboxylation and decarbonylation and the aqueous phase which is the product obtained after dehydration. The extent of the products obtained, such as the aqueous phase and the gases from the catalytic cracking over different catalysts can used to select the best suitable catalyst for the upgrading of the bio-oil.

Table 3: Product Distribution after Upgrading the Model Bio-Oil of Three Different Types of Catalysts

Catalyst Type	OLP (wt%)	Aqueous Phase (wt%)	Gases (wt%)
HZSM-5	61.08	18.95	19.97
HY	64.62	18.04	17.34
H-Mordenite	64.43	17.25	18.32

3.2.1. Aqueous Phase

The aqueous phase formation from dehydration is the major route for the deoxygenation in the upgrading of the bio-oil. From Table (**3**), it can be seen that the aqueous fraction produced by HZSM-5 is the highest as compared to the other catalysts. As earlier discussed, HZSM-5 has a uniform pore size as well as a smaller surface area as compared to the HY and H-Mordenite catalysts. In case of large pore sized catalysts, during the upgrading process, a large number of reactant molecules can easily pass through the supercages and do not undergo the reaction and remain unconverted [29]. In the case of HZSM-5, it possesses the uniform pore size which allows the reactant to react and be easily transformed with the help of the active sites of the catalyst. As based on SiO_2/Al_2O_3, the ratio for HZSM-5 is higher than for H-Mordenite which indicates the more acidic strength in HZSM-5 due to which, the amount of the hydroxyl group with the organic compounds are eliminated and this causes dehydration. This was also reported by Ben *et al*. [30]. They reported that the higher Al_2O_3 ratio led to the elimination of the methoxy group, ether bond and dehydration of the aliphatic and aromatic hydroxyl groups with the upgrading bio-oil process. Further on, Guo *et al*. [31] studied the performance of the catalyst for upgrading the bio-oil. They reported that the HZSM-5 caused the formation of the maximum aqueous phase which was the main deoxygenation route. Adjaye*et al*. [32] reported that HZSM-5 was the most suitable dehydrating catalyst as compared to the HY, H-Mordenite and silica-alumina catalysts.

3.2.2. Gaseous Phase

The gaseous product is the final product obtained from the upgrading process. Cracking caused the formation of gases which is considered to be the efficient deoxygenating route. As listed in Table (**3**), HZSM-5 tended to produce gaseous products in a higher fraction as compared to the other two catalysts. Gases were formed mainly due to decarboxylation and decarbonylation which resulted in the CO and CO_2

formation. Due to the bio-oil being deficient in the hydrogen, minor traces of the hydrogen has also been detected. Guo *et al*. [31] observed a similar kind of observation for HZSM-5 as a catalyst for upgrading the bio-oil as an efficient catalyst for promoting decarbonylation and decarboxylation reactions as compared to other zeolite-based catalysts. Adjaye *et al*. [32] showed that the gaseous products resulting from the catalytic upgrading of bio-oil were mainly carbon oxides. Furthermore, HZSM-5 was considered to be the most efficient catalyst from among the H-Mordenite, silica-alumina and HY catalysts.

3.2.3. Organic Liquid Product (OLP)

The Organic Liquid Product (OLP) is of main interest after the catalytic upgrading of the bio-oil. The detailed analysis of the OLP obtained is shown in Table (**4**) which involved the elemental analysis and the calorific value obtained by the three catalysts. It can be seen that the yield of OLP was low for HZSM-5 as compared to HY and H-Mordenite. This could be related to the quality of OLP. In the presence of HZSM-5 which involved evenly distributed surface area particles and a uniform pore size, it allowed more conversion of the oxygenated particles due to which efficient dehydration, decarboxylation and decarbonylation occurred. Meanwhile, efficiency and more conversions in the presence of HZSM-5 reduced the yield of OLP by increasing the amount of gas and aqueous product formation. Due to the efficient removal of oxygen content by using HZSM-5, the formation of hydrocarbons from oxygenated compounds were the result, and the end product, OLP, obtained had a better quality based on the high calorific value as shown in Table (**4**).The quality of OLP can also be examined from the calorific value as shown in Table (**4**). The energy density of OLP obtained after the catalytic cracking in the presence of HZSM-5 was higher as compared to HY and H-Mordenite. Furthermore, one can consider that HY has a surface area higher than that of HZSM-5 but, the SiO_2/Al_2O_3 is the same for both. Though it can be considered that there is no doubt that SiO_2/Al_2O_3 had an influence over the upgrading of the bio-oil as mentioned by Vitolo *et al*. [10]. They mentioned that the pore size affected the reaction occurrence the mostdue to the catalyst. However, if the reactants did not interact with the active sites of the catalyst, there would be no conversion. Similarly, H-Mordenite with the highest pore size but being less crystalline in nature from among all three catalysts allowed for less interaction of the reactants with the active sites of the catalyst. Moreover, it was observed to be a less efficient catalyst in terms of upgrading the bio-oil.

From Table (**4**), it can be observed that the OLP obtained after using HZSM-5 as a catalyst had a higher carbon content and the least oxygen content. This revealed the high calorific value of OLP, and HZSM-5 proved to be the best among the other catalysts. The carbon content of the product OLP obtained from upgrading in the presence of the H-Mordenite catalyst was low as compared to others but it had a high oxygen content which led to the observation that there was less conversion of the oxygenated compounds and thus the calorific value of the product was also low. The HY catalyst gave an OLP with a higher calorific value as compared to H-Mordenite catalyst. The amount of hydrocarbons formed was 16.27 wt % of OLP for HZSM-5 but for HY and H-Mordenite they were 15.16 wt % and 14.954 wt % of OLP, respectively. The high percentage of hydrocarbon formation by using HZSM-5 can be related to the pore size, pore volume, SiO_2/Al_2O_3 and the acidic strength of the catalyst. So, the DOD of the OLP obtained after upgrading the model bio-oil in the presence of HZSM-5, HY and H-Mordenite was 45.57%, 40.87% and 39.07%, respectively. HZSM-5 proved its effectiveness as the best deoxygenating catalyst.

CONCLUSIONS

In this study, bio-oil was upgraded by catalytic cracking in a continuous reactor over three different

Table 4: Elemental Analysis and Gross Calorific Value of the OLP Obtained by the Catalytic Cracking of the Model Bio-Oil over Three Different Catalysts

Catalyst Type	Carbon (wt %)	Hydrogen (wt %)	Nitrogen (wt %)	Oxygen (wt %)	Gross Calorific Value (kJ/g)
HZSM-5	67.41	6.12	0.16	26.29	30.321
HY	65.36	5.93	0.14	28.57	29.159
H-Mordenite	64.12	6.25	0.19	29.44	28.127

catalysts HY, H-Mordenite and HZSM-5. The catalysts used for cracking proved its effectiveness based on the observed conversion of model compounds and improved properties of bio-oil. The most effective catalyst based on the quality of end product was HZSM-5. Hydrocarbons formed was 16.27, 15.16, 14.954 wt % of OLP by using HZSM-5, HY and H-Mordenite, respectively. The high percentage of hydrocarbon formation by using HZSM-5 can be related to the pore size, pore volume, SiO_2/Al_2O_3 and the acidic strength of the catalyst. The DOD of the OLP obtained after upgrading the bio-oil in the presence of HZSM-5, HY and H-Mordenite was 45.57%, 40.87% and 39.07%, respectively.

REFERANCES

[1] Crocker M and R Andrews.Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals.Cambridge: Royal Society of Chemistry, 2010. http://dx.doi.org/10.1039/9781849732260

[2] Luque R, Campelo J, and Clark J. Handbook of Biofuels Production.Cambridge: Woodhead Publishing, 2010.

[3] Peters B. Thermal Conversion of Solid Fuels.United Kingdom: WIT Press, 2003.

[4] Zhang Q, Chang J, Wang, and Xu Y. Upgrading Bio-oil over Different Solid Catalysts. Energy & Fuels. 2006; 20: 2717-2720. http://dx.doi.org/10.1021/ef060224o

[5] Satterfield CN. Heterogenous Catalyst in Industrial Practice.Florida: Krieger, 1991.

[6] Mohan D, Pittman CU, and Steele PH. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. Energy & Fuels 2006; 20: 848-889. http://dx.doi.org/10.1021/ef0502397

[7] Xiu S and Shahbazi A. Bio-oil production and upgrading research: A review. Renewable and Sustainable Energy Reviews. 2012; 16: 4406-4414. http://dx.doi.org/10.1016/j.rser.2012.04.028

[8] Zhang Q, Chang J, Wang T, and Xu Y. Review of biomass pyrolysis oil properties and upgrading research. Energy Convers. Manage 2007; 48: 87-92. http://dx.doi.org/10.1016/j.enconman.2006.05.010

[9] Williams PT and Horne PA. Characterisation of oils from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading. Biomass and Bioenergy 1994; 7: 223-236. http://dx.doi.org/10.1016/0961-9534(94)00064-Z

[10] Vitolo S, Seggiani M, Frediani P, Ambrosini G, and Politi L. Catalytic upgrading of pyrolytic oils to fuel over different zeolites. Fuel 1999; 78: 1147-1159. http://dx.doi.org/10.1016/S0016-2361(99)00045-9

[11] Anex RP, Aden A, Kazi FK, Fortman J, Swanson RM, Wright MM, *et al*. Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways. Fuel 2010; 89, Supplement 1: S29-S35. http://dx.doi.org/10.1016/j.fuel.2010.07.015

[12] Guo Z, Wang S, Cai Q, Guo Z, Wang Y, and Wang X, "Catalytic cracking characteristics of bio-oil molecular distillation fraction " in World Renewble Energy Congress Sweden, 2011. http://dx.doi.org/10.3384/ecp11057552

[13] Abdullah N, Sulaiman F, and Gerhauser H. Characterisation of Oil Palm Empty Fruit Bunches for Fuel Application. Journal of Physical Science 2011; 22: 1-24.

[14] Gagnon J and Kaliaguine S. Catalytic hydrotreatment of vacuum pyrolysis oils from wood. Industrial & Engineering Chemistry Research 1988; 27: 1783-1788. http://dx.doi.org/10.1021/ie00082a008

[15] Gutierrez A, Kaila R, and Krause O. Hydrodeoxygenation of guaiacol as model compound for pyrolysis oil on noble metal catalysts 2008;

[16] Gutierrez A, Kaila RK, Honkela ML, Slioor R, and Krause AOI. Hydrodeoxygenation of guaiacol on noble metal catalysts. Catalysis Today 2009; 147: 239-246. http://dx.doi.org/10.1016/j.cattod.2008.10.037

[17] Hew KL, Tamidi AM, Yusup S, Lee KT, and Ahmad MM. Catalytic cracking of bio-oil to organic liquid product (OLP). Bioresour. Technol 2010; 101: 8855-8858. http://dx.doi.org/10.1016/j.biortech.2010.05.036

[18] Adjaye JD and Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts. Fuel Process Technol 1995; 45: 161-183. http://dx.doi.org/10.1016/0378-3820(95)00034-5

[19] Nokkosmäki MI, Kuoppala ET, Leppämäki EA, and Krause AOI. Catalytic conversion of biomass pyrolysis vapours with zinc oxide. J Anal Appl Pyrolysis 2000; 55: 119-131. http://dx.doi.org/10.1016/S0165-2370(99)00071-6

[20] Park H, Jeon JK, Suh D, Suh YW, Heo H, and Park YK. Catalytic Vapor Cracking for Improvement of Bio-Oil Quality. Catalysis Surveys from Asia 2011; 15: 161-180. http://dx.doi.org/10.1007/s10563-011-9119-7

[21] Lu Q, Li WZ, and Zhu XF. Overview of fuel properties of biomass fast pyrolysis oils. Energy Convers Manage 2009; 50: 1376-1383. http://dx.doi.org/10.1016/j.enconman.2009.01.001

[22] Guo ZW, Shurong Yin, Qianqian Xu, Guohui Luo, Zhongyang Cen, Kefa Fransson, Torsten H. Catalytic cracking characteristics of bio-oil molecular distillation fraction. Journal of Energy and Power Engineering 2011;Volume 34:

[23] Guo X, Zheng Y, Zhang B, and Chen J. Analysis of coke precursor on catalyst and study on regeneration of catalyst in upgrading of bio-oil. Biomass and Bioenergy 2009; 33: 1469-1473. http://dx.doi.org/10.1016/j.biombioe.2009.07.002

[24] Gayubo AG, Aguayo AT, Atutxa A, Prieto R, and Bilbao J. Deactivation of a HZSM-5 Zeolite Catalyst in the Transformation of the Aqueous Fraction of Biomass Pyrolysis Oil into Hydrocarbons. Energy and Fuels 2004; 18: 1640-1647. http://dx.doi.org/10.1021/ef040027u

[25] Sheng Q, Ling K, Li Z, and Zhao L. Effect of steam treatment on catalytic performance of HZSM-5 catalyst for ethanol dehydration to ethylene. Fuel Process Technol 2013; 110: 73-78. http://dx.doi.org/10.1016/j.fuproc.2012.11.004

[26] Lu R, Tangbo H, Wang Q, and Xiang S. Properties and Characterization of Modified HZSM-5 Zeolites. Journal of Natural Gas Chemistry 2003; 2: 56-62.

[27] Cui Q, Zhou Y, Wei Q, Tao X, Yu G, Wang Y, and Yang J. Role of the Zeolite Crystallite Size on Hydrocracking of Vacuum Gas Oil over NiW/Y-ASA Catalysts. Energy Fuels 2012; 26: 4664-4670. http://dx.doi.org/10.1021/ef300544c

[28] Sombatchaisak S, Praserthdam P, Chaisuk C, and Panpranot J. An Alternative Correlation Equation between Particle Size and Structure Stability of H-Y Zeolite under Hydrothermal Treatment Conditions. Industrial & Engineering Chemistry Research 2004; 43: 4066-4072. http://dx.doi.org/10.1021/ie049847k

[29] Komatsu T, "Catalytic cracking of paraffins on zeolite catalysts for the production of light olefins," in 20th Annual Saudi-Japan Symposium, Saudia Arabia, 2010.

[30] Ben H and Ragauskas AJ. Influence of Si/Al Ratio of ZSM-5 Zeolite on the Properties of Lignin Pyrolysis Products. ACS Sustainable Chemistry & Engineering 2013; 1: 316-324. http://dx.doi.org/10.1021/sc300074n

[31] Xiao-ya G, Yong-jie Y, and Ting-chen L. Influence of Catalyst Type and Regeneration on Upgrading of Crude Bio-oil through Catalytic Thermal Cracking. The Chinese Journal of Process Engineering 2004; 4: 53-58.

[32] Adjaye JD and Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways. Fuel Process Technol 1995; 45: 185-202. http://dx.doi.org/10.1016/0378-3820(95)00040-E

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