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Bio oil Production from Biomass using Pyrolysis and Upgrading - A Review

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Abstract: The Bio oil production from biomass has been witnessed a booming interest in recent years, due to the increased cost of fuel and the need to produce alternative fuels. This review discusses related issues and main approaches to Bio oil production from biomass. The main focus of the paper is to review the various work carried on feed stock of biomass in prolysis method, types of reactor and upgrading the bio oil. The feed stock related issues discussed are the particle size and characterization analysis by proximate and ultimate method. The review also concentrates on various characteristics of fast and slow pyrolysis such as temperature range, heating rate, nitrogen gas flow rate, and oil yield. Hydrodeoxygenation, hydrogenation and catalytic cracking are reviewed in upgrading. This paper will help the researchers in the field of alternate fuels to analyze the state of art method. **Keywords:** Bio oil, Biomass, Pyrolysis and Upgrading.

1. Introduction:

The diesel engines dominate the field of commercial transportation and agricultural machinery due to its ease of operation and higher fuel efficiency. The consumption of diesel is 4-5 times higher than petrol in India [2]. Due to the shortage of petroleum products and its increasing cost, efforts are on to develop alternative fuels especially, to the diesel oil for fully or partial replacement. Biomass can generally be defined as any hydrocarbon material which mainly consists of carbon, hydrogen, oxygen and nitrogen. Sulfur is also present in less proportions. Some biomass types also carry significant proportions of inorganic species. The concentration of the ash arising from these inorganics changes from less than 1% in softwoods to 15% in herbaceous biomass and agricultural residues. Biomass resources include various natural and derived materials, such as woody and herbaceous species, wood wastes, bagasse, agricultural and industrial residues, waste paper, municipal solid waste, sawdust, bio solids, grass, waste from food processing, animal wastes, aquatic plants and algae etc. Hydrocarbons can be produced from biomass via biological, biochemical, and thermo chemical processes as shown in Figure 1 [1].

Pyrolysis is touted to be one of the most promising thermo chemical technologies with the potential to convert cheap, local, and abundant lignocellulosic biomass such as grasses and trees into a useful form [3-5], and commercial scale plants, such as Kior in Mississippi, have begun construction and operations. Thermal technologies include direct combustion, gasification, liquefaction, and pyrolysis, all of which have the benefit of using lignocellulosic materials. Only pyrolysis and liquefaction produce a liquid product, and although recent work on liquefaction has shown promising results [6-8], it is currently a nascent technology with high capital costs due to the high pressures required. Pyrolysis has the advantage of low capital investment and a liquid final

product that can be transported and converted via catalysis to fuels and valuable products such as food flavorings, fertilizers, resins, and other specialty chemicals that are fully compatible with existing petroleum infrastructure [10].



Figure 1. Schematic of biomass conversion technologies [1].

Bio-oil from biomass fast pyrolysis is mainly produced from biomass residues in the absence of air at atmospheric pressure, a low temperature (450–550 °C), high heating rate (103–104 K/s) and short gas residence time to crack into short chain molecules and be cooled to liquid rapidly. Fast pyrolysis, an effective biomass conversion with high liquid yield, as much as 70–80% and a high ratio of fuel to feed, is regarded as one of the reasonable and promising technologies to compete with and eventually replace non-renewable fossil fuel resources [9].

2. Reactor type:

Several Kinds of reactors are used in the fast pyrolysis system like Bubbling fluidized bed, Circulating fluidized beds/transport reactor, Rotating cone pyrolyzer, Ablative pyrolyzer, Vacuum pyrolysis, Auger reactor, Heinze-type reactor, and Fixed bed. Similarly in slow pyrolysis system Tubular reactor and Microwave. An overview of the work done in the fast and slow pyrolysis system is shown in Table 1. This table represents a sample of work done and some works published on the topic of pyrolysis.

2.1 Fast pyrolysis

This section reviews various fast pyrolysis reactors used in this field of research.

2.1.1 Heinze-type reactor:

Ayse E. (2005) [10] the pyrolysis of cotton stalk was studied for determining the main characteristics and quantities of liquid and solid products. Particular variables investigated were temperature (from 400 °C to 700 °C), particle sizes (from 0.25 mm to 1.8 mm) and nitrogen gas flow rate (from 50 and 400 cm³/min). All experiments were performed at a heating rate of 7 °C/min. The characteristic of char is dependent on the pyrolysis conditions. Both the hydrogen and oxygen contents of char decrease as the temperature is increased. H/C ratio decreases 0.49 at 400 °C to 0.15 at 700 °C, indicating an increase in the aromaticity and carbonaceous nature of char.

2.1.2 Bubbling fluidized bed:

Hyun Ju (2008) [11] pyrolysis, the TG curves of Japanese larch exhibited a weight loss regime, completing the decomposition between 250 and 380 °C. The apparent activation energies ranged from 220 to 1009 kJ mol⁻¹, which changed with the level of conversion. The pre-exponential factor assuming an overall 0th,

1st, and 2nd order reaction ranged from 1012 to 1020 s⁻¹ for the decomposition of hemicellulose and cellulose in Japanese larch.

2.1.3 Fluidized bed:

Zheng Ji-lu (2008) [12] Cotton stalks can be pyrolyzed into bio-oil. The yield of bio-oil first increases and then decreases as a function of temperature. Therefore, there is an optimum temperature for pyrolysis from cotton stalks into bio-oil. The maximum yield for cotton stalks is 55% at 510 °C. The bio-oil is a complicated organic compound that consists mainly of water, acids and heterocyclic substances.

GUO Xiujuan (2011) [13] A continuous fluidized bed reactor with a capacity 5 kg·h⁻¹ was established and described previously. The important operation conditions were pyrolysis temperature (450-550 °C), gas residence time (less than 1 s), and condenser system. The ground, air-dried particles of rice husk with the size of 0.45 to1 mm were used in all experiments. Rice husk has a high ash content in proximate analysis and corresponding high acid-insoluble ash content in compositional analysis. The contents of cellulose and lignin are lower than wood materials, but the content of hemi-cellulose is higher.

2.1.4 Fixed bed:

Eylem P (2011) [14] Potato skin, a food industry waste, was pyrolysed under three different atmospheres namely static, nitrogen, and steam to produce bio-oil and its derivatives. The 316 stainless steel retort used in this study has a volume of 400 cm³ and externally heated by an electric furnace with the temperature being controlled by a thermocouple inside the bed. The oil yield obtained at 550 °C was 24.77% in static atmosphere, whereas it reached to 27.11% in nitrogen atmosphere.

Alina Rahayu Mohamed (2013) [15] The abundance of empty fruit bunch (EFB) was generated over time as the by-products during oil palm fresh fruit bunches processing for the production of crude palm oil. The EFB was viewed as renewable energy resources. In this study, two series of the EFB pyrolysis experiments were conducted using a fixed-bed reactor to determine the effects of holding time and the sweeping nitrogen gas flow rates on the pyrolysis yields. In each experiment, the pyrolysis temperature was raised to 442.15 °C with a heating rate of 50 °C/min and nitrogen flow rate of 150 cm³/min. The first series of experiment was conducted to determine the effect of holding time on the distribution of pyrolysis products. Therefore, the holding time was varied at 6, 8, 10 and 12 minutes. It was identified that at 10 minutes holding time, the highest bio-oil yield of 45.72% was obtained with bio-char yield of 25.88% and 28.40% gas produced. In the second series of experiments, the effect of nitrogen flow rates was investigated by varying the nitrogen flow rates at 150, 200, 300, 400 and 500 cm³/min. It was identified that at nitrogen flow rates of 200 cm³/min, the bio-oil yield of 46.02% was at its maximum with bio-char and gas production of 26.69% and 27.29% respectively.

2.2 Slow pyrolysis:

Various works has been carried out using slow pyrolysis system. This section reviews various slow pyrolysis reactors used in this field of research.

2.2.1 Tubular reactor:

F. Karaosmanoglu (1999) slow pyrolysis of the straw and stalk of the rapeseed plant was investigated within a tubular reactor under the conditions of static atmosphere, varying temperatures of 350 °C, 450 °C, 550 °C and 650 °C and at heating rates of 10 °C/ min and 30 °C/min. The maximum liquid yield was observed to be evolving at 650 °C pyrolysis temperature and at a heating rate of 30 °C/min. This oil, which is quite viscous at room temperature and containing no water, is a mixture of aliphatic and aromatic hydrocarbons having an empirical formula of $CH_{1.39} O_{0.46} N_{0.02}$, H/C molar ratio, O/C 1.39 mole ratio 0.46 and a heating value of 27.15 MJ/kg. It contains ash, sulphur and nitrogen in very small ratios.

2.2.2 Fixed bed:

Scott Grierson (2009) [18] Aquatic microalgae have high potential for production of bio-chemicals, liquid transport fuels and charcoal. The samples were first analysed with a Computer Aided Thermal Analysis (CATA) technique at a standard heating rate of 10 °C /min. For all species, the energy required to achieve thermal conversion was found to be approximately 1 MJ/kg. Gas chromatography was then applied to measure

the evolution of biogas compounds with temperature. The heat of combustion of the biogas compounds was estimated to vary significantly between species, ranging from 1.2 to 4.8 MJ/kg. Pyrolysis oil product yields were also estimated at 500 °C.

2.2.3 Microwave:

Sharifah Mona Abdul Aziz (2013) [19] Pyrolysis of palm kernel shell (PK), wood chips (WC) and sago wastes (SW) was performed on microwave irradiation at different heating time, at moderate temperature 250–390 °C. Samples were placed in quartz reactor and subjected to microwave heating in inert atmosphere to afford bio-oils (PKO, WCO and SWO). The highest calorific values recorded are 27.19 MJ/kg, 25.99 MJ/kg, and 21.99 MJ/kg for PKO, WCO and SWO. FTIR spectroscopy showed the presence of functional groups such as phenol, alcohols, ketones, aldehydes and carboxylic acids. The GCMS showed that PKO, WCO and SWO consist of significant quantities of potentially high value hydrocarbons such as monoaromatic hydrocarbons and phenolic compounds. Importantly, the bio-oils do not contain carcinogenic polyaromatic hydrocarbons (PAH). Upon further refining, the bio-oils have a potential as valuable source for fuel or chemical feed stocks.

| Reference | Type Of Pyrolysis | Reactor Type | Temperature Range | Heating RateN2 Flow RateBiomass Type | | Partial Size | Yield | Best Parameter | |
|-----------|----------------------|---|--|--|--|--|----------------------|--|--|
| [17] | Slow pyrolysis | tubular reactor | 350 °C, 450 °C, 550 °C and 650 °C | 10 °C /min and 30 °C /min | - | straw and stalk of the rapeseed plant | 0.5–1.0 mm | 35% | 35% at 650 °C in 30 °C /min. |
| [10] | Fast pyrolysis | Heinze-type reactor | 400 °C to 700 °C | 7 °C /min | 50 and 400 cm3/min | cotton stalk | 0.25 mm to 1.8 mm | 23.82% | 23.82% at 550 °C, in 1.85 mm. 100 cm ³ /min |
| [11] | Fast pyrolysis | 316 stainless steel bubbling fluidized bed | 200 to 500 °C, | 5–20 °C/min | - | Japanese larch sawdust | 0.2 to 1.18 mm, | 55% | |
| [12] | Fast pyrolysis | fluidized bed | 480 to 530 °C | - | - | cotton stalk | 0.55-1.6 mm | 55% | 55 wt% at 510 °C |
| [18] | Slow pyrolysis | fixed bed | 220 °C- 750°C | 10 °C/min. | - | microalgae | - | 38% - 48% | 48% at 500 °C |
| [13] | Fast pyrolysis | fluidized bed | 450 to 550 °C | 35°C /min | - | Rice husk | 0.45-1 mm | 46.36% | 46.36% at 550 °C |
| [14] | Fast pyrolysis | 316 stainless steel fixed bed with electric heater | 400, 450, 500, 550, 600, and 700 °C | 5 °C min-1 with a constant | 50, 100, 200 and 400 cm ³ min-1 | Potato skin | 0.81 mm | 18.60% - 27.11% | 27.11% at 550 °C in 200 cm ³ min–1. |
| [15] | Fast pyrolysis | 316 stainless steel fixed bed with electric heater | From room temperature to 442.15 °C | 50 °C /min | 1 50, 200, 300, 400 and 500 cm ³ min-1 | empty fruit bunch | 710-1000 μm | 37.08% - 46.02% | 46.02% at 442.15°C in 200 cm ³ min-1 |
| [19] | Slow pyrolysis | microwave | 250 °C –390 °C | 5 °C/min. | 500 ml/min | palm kernel shell (PK), wood chips (WC) and sago wastes (SW) | _ | 14.65% (PK) 13.86% (WC) 16.51% (SW) | 14.65% for PK, 13.86% for WC, 16.51% for SW at 390 °C. in 500 ml/min |

Table 1 Type of Reactor and biomass to produce bio-oil

3. Feedstock characterization:

3.1 Fuel size preparation:

J. M. Encinar etal (1996) [20] studied the olive and grape bagasse using as a feed stock to produce the bio oil by pyrolysis. Variables investigated were temperature between 300 and 900 °C and particle size between 0.4 and 2 mm diameter. Soybean cake, an agricultural by product, was selected as raw material for pyrolysis experiments Basak Burcu Uzun (2006) [21]. Soybean cake was ground in a high speed rotary cutting mill and screened to give fractions of 0.224 < Dp < 0.425 mm, 0.425 < Dp < 0.85 mm, 0.85 < Dp < 1.25 mm and 1.25 < Dp < 1.8 mm. The highest oil yield obtained was 42.83% with sweeping gas velocity of 200 cm³ min⁻¹, heating rate of 700 °C min⁻¹ and particle size range of 0.425 < Dp < 0.85 mm. The feedstock for experimental runs were rice straw, sugarcane bagasse and coconut shell and the samples that were ground in a rotary cutting mill were further screened into fractions of particle diameter <0.50 mm W.T. Tsai (2006) [22]. It was found that the yield of liquid tar product from sugarcane bagasse was higher than those of rice straw and coconut shell. Employing the higher pyrolysis temperature of >500 °C, faster heating rate of >200 °C/min, and longer holding time of >2 min, the pyrolysis tar yield reached a maximum of ca. 50%. A. kwasi etal (2007) [23] investigated the energy recovered from the switch grass and contained in the bio-oil produced was about 52%. The approximately 20 kg/h maximum feed rate to a variable speed controlled with an interchangeable diameter 1.6-2.5 cm.

3.2 Percentage of Bio oil yield:

Jale Yanik (2007) [24] fast pyrolysis of three biomass species (corncob, oreganum stalks and straw) was carried out at 500 °C. The gas products obtained with a yield around 30–40% were composed of mostly carbon oxides. Ozlem Onay (2007) [25] the air-dried biomass sample was milled, sieved and classified to obtain a fraction of uniform particle size. The air dried particle size between 0.85 and 1.25 mm sample is used in these experiments. The bio oil a yield is considers in three different modes for effect of heating rate, pyrolysis temperature and sweep gas velocity. The oil yield reaches a maximum of 54% at a final pyrolysis temperature of 600 °C, heating rate of 300 °C min⁻¹, and sweeping gas flow rate of 100 cm³ min⁻¹. Zheng Ji-lu (2008) [26] the yield of bio-oil first increases and then decreases as a function of temperature. Therefore, there is an optimum temperature for pyrolysis from cotton stalks into bio-oil. The maximum yield for cotton stalks is 55% at 510 °C. Charles A (2010) [27] Bio-oil and bio-char were produced from corn cobs and corn stover (stalks, leaves and husks) by fast pyrolysis using a pilot scale fluidized bed reactor. Yields of 60% (mass/mass) bio-oil (high heating values are 20 MJ kg⁻¹, and densities >1.0 Mgm⁻³) were realized from both corn cobs and from corn stover. Bio char yield was 18.9% and 17.0% (mass/mass) from corn cobs and corn stover, respectively. Faisal Abnisa (2011) [28] palm shell waste was pyrolyzed to produces bio-oil. The optimal conditions found to be at the temperature of 500 °C, N₂ flow rate of 2 L/min, particle size of 2 mm and reaction time of 60 min and yield of bio-oil was approximately obtained 46.4 wt %.

3.3 Bio oil heating value and composition:

J. M. Encinar etal (2000) [29] Pyrolysis of C. cardunculus L. leads to three phases solid, liquid and gaseous, whose yields are strongly dependent on temperature but practically independent of Particle size, nitrogen flow rate, and initial sample weight under the conditions of this study. The gas distribution varies notably with temperature, with increasing formation of H₂, CH₄, CO and CO₂. The liquid phase reaches a maximum yield at temperatures between 400 °C and 500 °C. The fluid bed fast pyrolysis system with continuous processing of microalgae feeds at a rate of 4 g min-1 Xiaoling Miao (2004) [30]. Bio oil has a higher heating value of 29 MJ/kg, which is about 1.4 times of that of wood and lower oxygen content. D. Ozcimen (2004) [31] the cold extraction pressing method is using to production of bio-oil and biochar from rapeseed cake. Rapeseed contains 79.44% volatile matter, 8.34% fixed carbon and 4.56% ash. The lower heating value of the rapeseed cake is 23.4 MJ/kg, while the gross heating value is 24.5 MJ/kg. The bulk density of the cake is 557 kg/m³. Su-Hwa Jung (2008) [32] Rice straw from a province in Korea was dried in air and cut into a rectangle. It was sieved to obtain particles with a mean size of 5 mm. The bamboo sawdust (P. bambusoides) from a bamboo sawmill had very fine particles. It was sieved, and particles with mean sizes of 0.6 and 0.85 mm were obtained. The volatile matter content of the rice straw was 82.8 wt%, and its ash content was fairly high at about 9 wt.%. The higher heating values of the rice straw and the bamboo sawdust were 16 and 17.7 MJ/kg, respectively. Table 2 summarise the proximate and ultimate analysis for various bio mass.

4. Upgrading

The addition of catalysts to the pyrolysis system enhances reactions that include cracking, decarbonylation, decarboxylation, hydrocracking, hydrodeoxygenation, and hydrogenation have been reported to take place for both zeolite cracking and HDO [40]. Examples of these reactions are given in Fig. 1.

| Cracking: | $R_1 \xrightarrow{CH_2} CH_2 \xrightarrow{CH_2} CH_2 \xrightarrow{R_2} \longrightarrow$ | $\mathbf{R}_{1}^{\mathbf{CH}} \mathbf{CH}_{2} + \mathbf{H}_{2}^{\mathbf{C}} \mathbf{CH}_{2}$ |
|---------------------|---|--|
| Decarbonylation: | $R_1 - C$ | R ₁ -H ⁺ CO |
| Decarboxylation: | $R_1 - C_{OH} \longrightarrow$ | R ₁ - H + CO ₂ |
| Hydrocracking: | $R_1 CH_2 CH_2^{R_2} + H_2 \longrightarrow$ | R_1 -CH ₃ + H ₃ C-R ₂ |
| Hydrodeoxygenation: | R—OH + H ₂ → | R—н + н ₂ о |
| Hydrogenation: | $\begin{array}{c} \mathbf{R}_{1} \\ \mathbf{C} = \mathbf{C} \\ \mathbf{H} \\ \mathbf{H} \\ \mathbf{H} \end{array} + \mathbf{H}_{2} \longrightarrow$ | $R_1 CH_2 CH_2 + H_2O$ |

Fig 1 Representative catalytic upgrading reactions [40]

| Characteristics | Moistur e | Ash | С | н | Ν | S | 0 | HV | Referen | |
|--------------------------------|--------------|-------|-------|------|------|------|--------|--------|---------|--|
| | (wt%) | | | | | | MJ/kg) | ce | | |
| Cardoon | 8.40 | | 42.78 | 4.40 | 0.64 | 0.09 | 43.69 | 18.20 | [29] | |
| C. protothecoides (microalgae) | 5.39 | 6.36 | 62.07 | 8.76 | 9.74 | - | 19.43 | 30 | [30] | |
| M. aeruginosa (microalgae) | 4.40 | 13.26 | 60.99 | 8.23 | 9.83 | - | 20.95 | 29 | | |
| Soybean cake | 9.15 | 6.15 | 52.46 | 6.17 | 8.72 | - | 26.51 | 23.23 | [21] | |
| Rice straw | 13.61 | 9.54 | 50.93 | 6.04 | 0.83 | 0.23 | 41.61 | 16.35 | | |
| Sugarcane bagasse | 16.07 | 4.34 | 58.14 | 6.05 | 0.69 | 0.19 | 34.57 | 18.61 | [22] | |
| Coconut shell | 11.26 | 3.38 | 63.45 | 6.73 | 0.43 | 0.17 | 28.27 | 22.83 | | |
| Switch grass | 2.65 | 2.54 | 46.27 | 6.63 | 0.50 | 0.00 | 41.41 | 17.935 | [23] | |
| Oreganum stalk | 6.3 | 2.1 | 42.90 | 6.40 | 0.6 | 0.29 | - | 25 | | |
| Corncob | 9.0 | 4.0 | 42.50 | 6.00 | 0.7 | 0.29 | - | 24 | [24] | |
| Straw | 7.2 | 4.1 | 43.89 | 6.54 | 0.42 | 0.51 | - | 19 | | |
| Bamboo sawdust | 7.3 | 1.7 | 46.90 | 5.85 | 2.11 | 0.22 | 47.02 | 17.7 | [32] | |
| Cotton stalk | 7.87 | 6.97 | 42.3 | 7.9 | 0.3 | 0.2 | 49.4 | 17.77 | [26] | |
| Corn cobs | | 1.94 | 55.14 | 7.56 | 0.56 | 0.05 | 36.9 | 19.5 | [27] | |
| Corn Stover | | 4.88 | 53.97 | 6.92 | 1.18 | 0.05 | 37.94 | 22.1 | [27] | |

Table 2 Proximate and ultimate analysis for various bio mass

4.1 Hydrodeoxygenation (HDS):

HDO is closely related to the hydrodesulphurization (HDS) process from the refinery industry, used in the elimination of sulphur from organic compounds. Both HDO and HDS use hydrogen for the exclusion of the heteroatom, forming respectively H_2O and H_2S . HDO is normally carried out at temperatures between 250°C and 450 °C [33]. As the reaction is exothermic and calculations of the equilibrium predicts potential full conversion of representative model compounds up to at least 600 °C, it appears that the choice of operating temperature should mainly be based on kinetic aspects. The effect of temperature was investigated by Elliott and Hart [34] for HDO of wood based bio-oil over a Pd/C catalyst in a fixed bed reactor at 140 bar. Here it was found that the oil yield decreased from 75% to 56% when increasing the temperature from 310 °C to 360 °C. This was accompanied by an increase in the gas yield by a factor of 3. The degree of deoxygenation increased from 65% at 310 °C to 70% at 340 °C. Above 340 °C the degree of deoxygenation did not increase further, but instead extensive cracking took place rather than deoxygenation. The observations of Elliott et al. [34] are due to the reactivity of the different types of functional groups in the bio-oil [35]. Temperatures range from 250 to 450 °C. Coke formation generally increases with time and temperature, as does deoxygenation.

4.2 Zeolite cracking:

Catalytic upgrading by zeolite cracking is related to fluid catalytic cracking (FCC), where zeolites are also used. Compared to HDO, zeolite cracking is not as well developed at present, partly because the development of HDO to a large extent has been extrapolated from HDS. It is not possible to extrapolate zeolite cracking from FCC in the same degree [33]. Williams et al. [36] investigated the effect of temperature on HZSM-5 catalysts for upgrading of bio-oil in a fixed bed reactor in the temperature range from 400 to 550 °C. An increased temperature resulted in a decrease in the oil yield and an increase in the gas yield. This is due to an increased rate of cracking reactions at higher temperatures, resulting in the production of the smaller volatile compounds. However, in order to decrease the oxygen content to a significant degree the high temperatures were required. In conclusion, it is crucial to control the degree of cracking. A certain amount of cracking is needed to remove oxygen, but if the rate of cracking becomes too high, at increased temperatures, degradation of the bio-oil to light gases and carbon will occur instead. Experimental zeolite cracking of bio-oil has shown yields of oil in the 14–23 wt% range [37]. This difference is due to pronounced carbon formation in the system during operation, constituting 26–39 wt% of the product.

4.3 Ceria-zirconia:

Catalytic strategy to upgrade the light fraction of a simulated bio-oil, consisting of acetic acid, acetol, and furfural. The acid content of the feed was significantly reduced by ketonization at 623 K over a ceria– zirconia (CeZrOx) mixed oxide catalyst. The presence of furfural decreased the ketonization activity; however, it was possible to regain the initial catalytic activity by removal of furfural from the feed. Acetol was highly reactive over the mixed oxide, and its presence did not influence the ketonization activity [38]. The results from reaction kinetics measurements for conversion of acetol suggest that the primary products are pyruvaldehyde and 1,2-propylene glycol formed by transfer hydrogenation. These two primary products then undergo reactions in series and parallel to produce an array of C_3 – C_6 carbonyl compounds, constituting an upgraded intermediate feed appropriate for further processing steps to obtain transportation fuel components.

4.4 Pt/Al₂O₃ catalyst:

Bio-oil was studied over a series of supported Pt catalysts. Pt/Al_2O_3 showed the highest activity for deoxygenation, the oxygen content of the model oil decreasing from an initial value of 41.4 wt% to 2.8 wt% after upgrading. GC–MS analysis of the oil showed it to be highly aromatic, the major components corresponding to alkyl-substituted benzenes and cyclohexanes. CO_2 was formed as the major gaseous product, together with lower yields of H_2 and C_1 – C_6 hydrocarbons [39].

4.5 Mo–10Ni/γ-Al₂O₃ catalyst

The raw bio-oil was produced by vacuum pyrolysis of pine sawdust. The optimal production conditions were investigated. A series of nickel-based catalysts were prepared. Their catalytic activities were evaluated by upgrading of model compound (glacial acetic acid). Results showed that the reduced Mo–10Ni/ γ -Al₂O₃ catalyst had the highest activity with the acetic acid conversion of 33.2% [41]. Upgrading of the raw bio-oil was investigated over reduced Mo–10Ni/ γ -Al₂O₃ catalyst. After the upgrading process, the pH value of the bio-oil increased from 2.16 to 2.84. The water content increased from 46.2 wt.% to 58.99 wt.%. The H element content

in the bio-oil increased from 6.61 wt.% to 6.93 wt.%. The dynamic viscosity decreased a little. The results of GC–MS spectrometry analysis showed that the ester compounds in the upgraded bio-oil increased by 3 times. It is possible to improve the properties of bio-oil by hydro treating and esterifying carboxyl group compounds in the bio-oil.

5. Conclusion:

Bio-oil is recognized as alternative petroleum based fuel. Pyrolysis is now accepted as a technology for producing high yields of liquid fuels that can be used in many applications as direct substitutes for conventional fuels or as a source of chemicals. This survey proves that the volatile matter and cellulose content had major influence on the bio oil yield. The bio-oil yields were increased gradually along with increase of the flow rate and the feeding rate. In future, more work is needed on further improving and refining techniques mentioned in this paper, and to deal with the problems that we have not anticipated. The success story of pyrolsis is also going to encourage an extension of its methods to bio oil production from biomass.

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