We are IntechOpen, the world's leading publisher of Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

BOOK CITATION INDEX

CLARIVATE ANALYTICS

INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Methods and Applications of Deoxygenation for the Conversion of Biomass to Petrochemical Products

Duminda A. Gunawardena and Sandun D. Fernando

Additional information is available at the end of the chapter

1. Introduction

Depleting reserves, uncertain economics, and environmental concerns associated with crude oil have prompted an extensive search for alternatives for producing transportation fuels. Biomass has been given close scrutiny due to the emphasis on climate change and the ability of biomass based energy systems to mitigate greenhouse gas (GHG) emissions. Further, its ability to produce fuels and chemicals that are identical to those produced using petroleum resources, makes biomass an important alternative raw material [1, 2]. Biomass can be considered clean, as it contains negligible amounts of sulfur and nitrogen. Consequently, the emissions of SO_2, NO_x are extremely low compared to conventional fossil fuels. The overall CO_2 emission is considered to be neutral, as CO_2 is recycled by the plants through photosynthesis [3]. Moreover, substitution of fossil fuels with biomass-based counterparts could lead to net CO_2 emission reductions [4].

1.1. Biomass production

Biomass encompasses all plant and plant-derived materials as well as animal matter and animal manure. Due to its abundance biomass has to be considered as a vital source of energy to satisfy the global energy demand. Table 1 shows the breakdown of primary energy sources and their contribution to total world energy demand during 1973 and 2009. It is evident that the contribution from biomass is only 10% over this period and in the global scale bioenergy has not yet made any significant impact. However, according to a report published by the United States Department of Agriculture, biomass derived energy has become the highest contributor among all the renewable sources during 2003. According to US statistics 190 million dry tons of biomass is consumed per year, which is equivalent to

3% of current energy consumption [5]. Even though it is hard to conceive that biomass can totally eliminate the use of fossil fuel consumption, it can complement the renewable energy sector together with other sources like wind, solar and geothermal energy.

Primary energy sources	1973	2009
The total world energy demand (Mtoe)	6111	12150
Oil	46.00%	32.80%
Natural gas	16.00%	20.90%
Nuclear	0.90%	5.80%
Hydro	1.80%	2.30%
Biofuels and waste	10.60%	10.20%
Coal / peat	24.60%	27.20%
other	0.10%	0.80%

Table 1. The world's primary energy sources with its contribution. [6]

1.2. Biomass to energy conversions

Biomass has been intimately connected with the everyday life of people since prehistoric times. With the advent of fire by rubbing splinters, humans began to exploit the chemical energy of biomass to produce heat. Ever since, various methods have been developed to convert chemical energy present in biomass to useful heat energy. These conversion methods can be summarized as shown in figure (1).
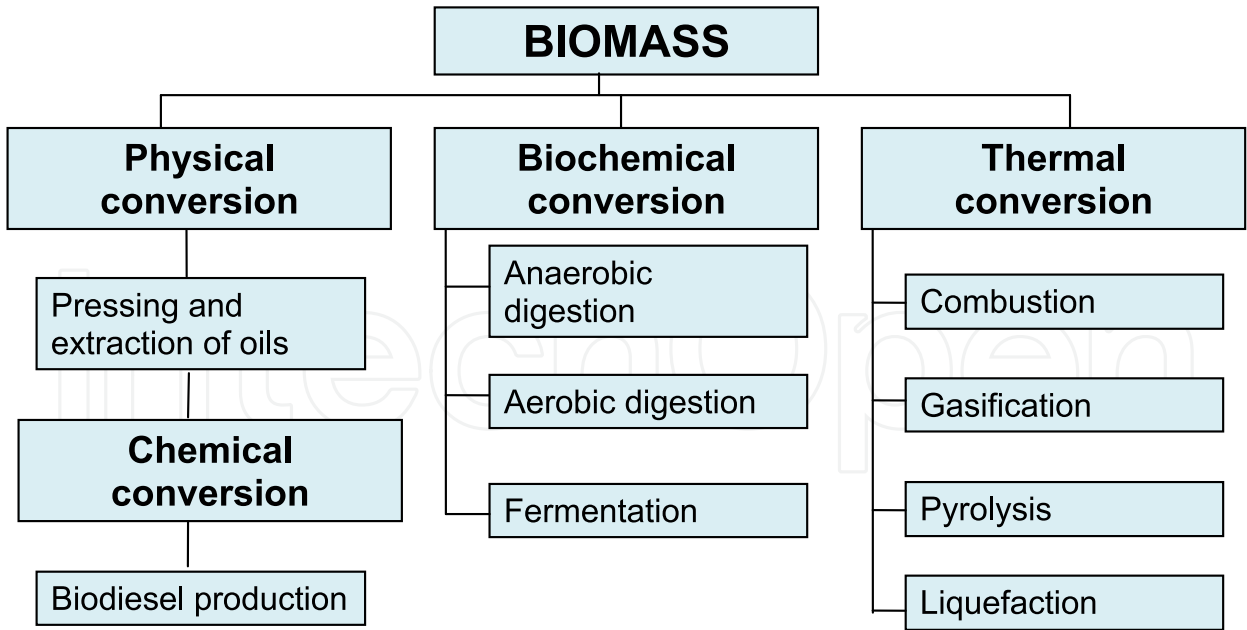

Figure 1. Different categories of biomass conversion

Physical conversion of biomass typically involves pressing the plant (or animal) matter to produce triglyceride oils. Triglycerides cannot be used directly as transport fuels and needs to be processed further. Triglycerides can be converted into a renewable fuel widely known

as biodiesel using the transesterification process. This process converts triglyceride in the presence of alcohol to fatty acid alkyl esters .

Biochemical conversion primarily involves using microorganisms or enzymes to breakdown complex chemicals present in biomass into simpler sugars or alcohols. Biomass conversion to alcohols such as ethanol has attracted wide interest in the recent past. The corn to ethanol technology is mature and is commercial in the US. Nevertheless, this technology has created some debate in the context that corn is still a primary food to many around the world. To circumvent this issue, significant strides have been made in the use of lingo-cellulosic biomass as a source for ethanol. In this method enzymes are used to breakdown cellulose to its monomers and subsequently subjected to fermentation under anaerobic conditions using microorganisms.

Thermochemical conversion is another key process that uses heat to induce chemical transformations in the biomass constituents to produce energetically useful intermediate and/or end products. Conversion techniques available under this umbrella can be categorized into four main processes as represented in figure (1). Energy generation by combustion of biomass can be considered as the most archaic [7]. However, increasing demand for transport fuels has led to the development of other processes that involve converting biomass into liquid and gaseous products [8] such as gasification, pyrolysis and liquefaction. Gasification is the conversion of biomass to a mixture of gases called synthesis gas (or syngas) that primarily consists of hydrogen, carbon monoxide, carbon dioxide and methane. During gasification, biomass is heated under an oxygen-lean environment [9]. Synthesis gas can be directly used in an internal combustion engine or can be converted to liquid fuels using a method known as Fisher-Tropsch (FT) synthesis [7, 10]. Fisher-Tropsch process is considered to be quite energy intensive and therefore, is not yet believed to be economical to compete with petroleum fuels. Nevertheless, active research is still in progress to improve the process [11, 12]. Fermentation of synthesis gas to alcohols (primarily ethanol) using microorganisms is also an active area of research [13].

Pyrolysis and liquefaction are two closely related routes targeted towards producing liquids – called bio-oil or bio-crude [14, 15]. Although not universally accepted, the term bio-oil generally refers to the highly oxygenated liquid product that directly exits a pyroloysis reactor. The term bio-crude represents a more deoxygenated liquid product.

Pyrolysis, unlike gasification, takes place in an oxygen-free atmosphere. The most common technique for producing a large volume of condensable fraction is the fast pyrolysis process. Several reactor configurations used for fast pyrolysis include: ablative, entrained flow, rotating core, vacuum pyrolysis, circulating fluidized bed, and deep bubbling fluidized bed reactors [16]. During fast pyrolysis, biomass is heated at a very high heating rate (eg. 10^3–10^4 K/s)[17]. The temperature at which the thermal scission of biomass material such as cellulose and lignin take place is around 450–550 °C. The bio-oil portion is originally in the vapor-phase and obtained by quenching the volatile output. The yields of the condensable-fraction are reported to be as high as 70–80%. According to some kinetics studies conducted for different biomass, the frequency factor for pyrolysis varies between 10^9-10^{11} orders of

magnitude. This is an indication of how fast the reaction would occur during a short residence time [18].

Since its chemical complexity, the biomass pyrolysis reaction has been studied by using model compounds like cellulose. A set of possible reactions paths under different heating conditions is presented in figure (2)[19, 20].

The composition of bio-oil is substantially different from crude petroleum due to the presence of high concentrations of oxygenates. Biomass to bio-oil pyrolysis stoichiometry can be represented using an empirical formula as shown in eq.(1).
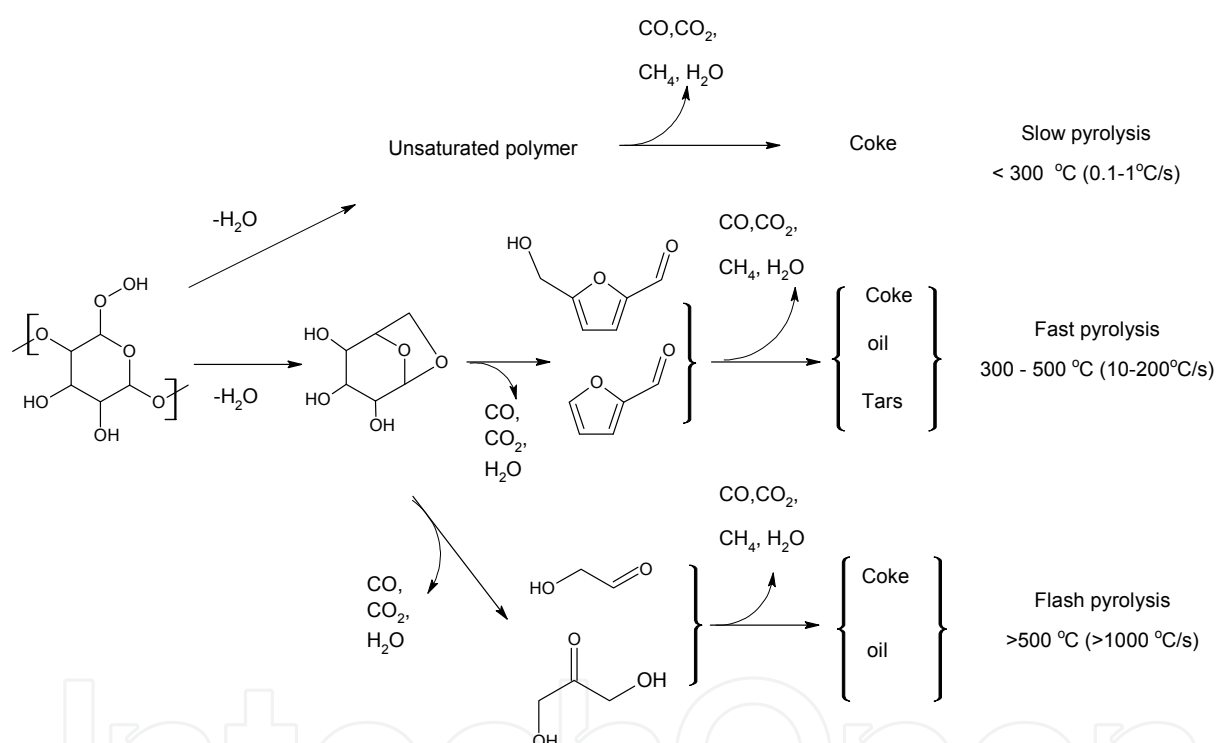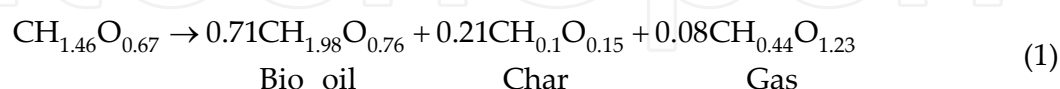
$$CH_{1.46}O_{0.67} \rightarrow \underset{\text{Bio oil}}{0.71CH_{1.98}O_{0.76}} + \underset{\text{Char}}{0.21CH_{0.1}O_{0.15}} + \underset{\text{Gas}}{0.08CH_{0.44}O_{1.23}} \tag{1}$$

Figure 2. Cellulose pyrolysis with the products at different heating conditions. (Information for scheme was adapted from Huber et al. [20])

Bio-oil properties are highly variable and depend heavily on the type of biomass. High fibrous biomass that contains high amounts of lignin is considered to be the most effective for the production of bio-oil for fuel applications. Further, the oil-yields and composition of bio-oils highly depend on the process (pyrolysis/ liquefaction) used. Fast pyrolysis yields higher amounts of bio-oil compared to slow pyrolysis whereas liquefaction produces low amounts of oxygenated compounds as compared to fast pyrolysis. Oxygenated compounds such as aldehydes, alcohols, ketones, and carboxylic acids can be seen in bio-oils in varying degrees. A typical product distribution of bio-oil is depicted in figure (4). It can be seen that bio-oil contains large amounts of ketones, carboxylic acids and aldehydes [22].
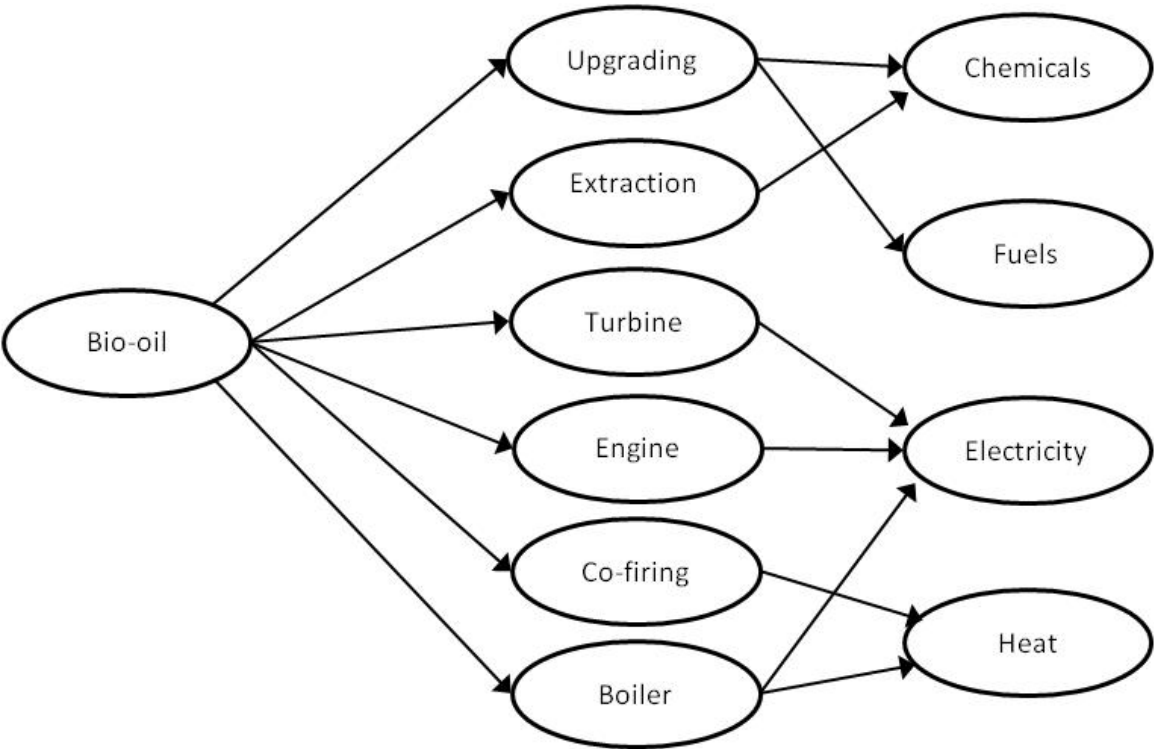
Figure 3. Different industrial applications of bio-oil derived from biomass (In formation adapted from Bridgwater et al. [21].)
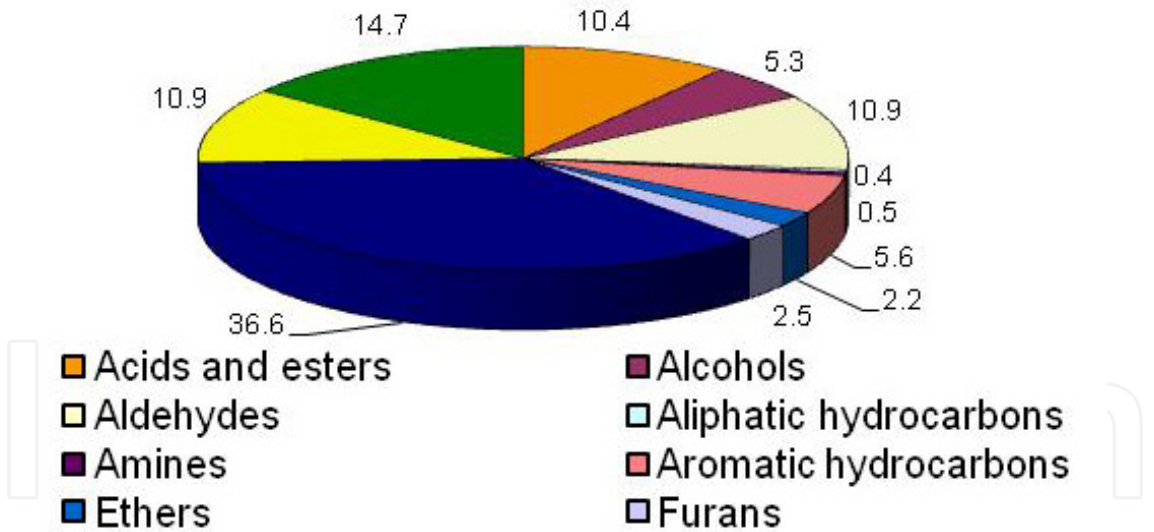

Figure 4. Relative distribution of chemical compounds in bio-oil (In formation adapted from Adjaye et al. [23].)

Bio-oil has already been tested in furnaces and gas turbines [21], as well as in space heaters and in boilers[24, 25], as represented in figure (3). Although bio-oil has potential as a crude-oil alternative, problems have been reported when bio-oil was used in such applications. These include, blocking filters by high levels of char particulates, high viscosity causing pumping issues, and corrosion from the low pH [26].

Liquefaction is another approach to producing bio-oils. The concept of oil production using biomass in hot water surfaced in the early 1920's. However, a more robust and effective method was not available until Pittsburg Energy Research Center (PERC) in the 70's demonstrated the use of carbon monoxide, steam and sodium carbonate catalyst at Albany Biomass Liquefaction facility in Oregon USA. Detailed information on this method can be found elsewhere [27].

The quality of bio-oil from the liquefaction process is reported to be superior to that obtained from pyrolysis. Liquefaction of biomass using super -critical methods can be considered as one of the more recent techniques under investigation.

Conversion of biomass to a product that is compatible with existing petroleum refinery infrastructure is prudent in several fronts. First, this will allow biomass to be converted into fuels and chemicals that are identical to what we use today (such as gasoline, diesel and jet fuels). So, such fuels could be used in present-day automobiles with no engine modifications. On the other hand, usage of existing fuel production and distribution of infrastructure helps long-term sustainability of biomass-to-fuels technology [28].

The challenge of converting bio-oil into a hydrocarbon fuel has been effective for the removal of functional groups that contain oxygenates (–OH, -COH, -COOH, etc.). The oxygen content of biomass-derived bio-oil is estimated to be 35-40% with a heating value between 16 and 19 MJ/kg [8]. In the recent years, there has been an unprecedented growth of research and developmental efforts related to conversion technologies and the information is scattered. Accordingly, the overall objective of this review is to assimilate this information and compare the status of key deoxygenation technologies.

2. Deoxygenation

The presence of oxygen in cellulose, hemicelluloses and lignin is the primarily reason for biomass derived bio-oil to be highly functionalized. Cellulose and hemicellulose have common structural building blocks which are glucose and xylose respectively. Cellulose which is the most abundant component in terrestrial biomass is a crystalline polymer, and therefore, is quite difficult to chemically transform. Lignin which is abundant in biomass is mainly an amorphous poly aromatic polymer. Because of this complex heterogeneity of biomass, the liquid derived from the pyrolysis or liquefaction process contains a variety of different chemical species which can be roughly estimated to be around 400.

2.1. Importance of deoxygenation

The properties of bio-oil are significantly affected by its chemical composition. Unlike crude petrolium, bio-oil constituents have numerous functional groups as shown in figure (4). The high functionality decreases the stability of the oils and results in polymerization. A direct consequence is the increase of viscosity of bio-oils with time which in turn raises concerns about the feasibility of using bio-oil products as substitutes for petrochemical fuels. In addition to instability, low pH values and the presence of a high water content and ash

content are considered problematic [29, 30]. Additionally, the presence of oxygenates and water in the bio-oil reduces the heating value. Consequently, upgrading is necessary to make it useful as a fuel.

As shown in the figure (5) upgrading improves the H/C molar ratio together with increasing the heating value. In contrast, crude petroleum is lean in oxygenated compounds and therefore, most of the chemistries developed to date are based on adding functional groups to increase its activity. As a result, there is only limited knowledge on techniques available to remove functionality from highly oxygenated compounds. However the upgrading of bio-oil by removing of oxygen (deoxygenation) is considered as one of the most intricate challenges we face today in getting bio-oil to a form that is applicable as a fuel intermediate.

As discussed above, chemical species present in biomass derived liquid bio-oil can be categorized into alcohols, aldehyde / ketones, carboxylic acids, phenols and furans. Therefore the upgrading process of bio-oil involves removal of various oxygenated species and can be collectively called as deoxygenation. The deoxygenation process predominantly involves three reaction classes, i.e., dehydration, decarbonilation and decarboxylation.
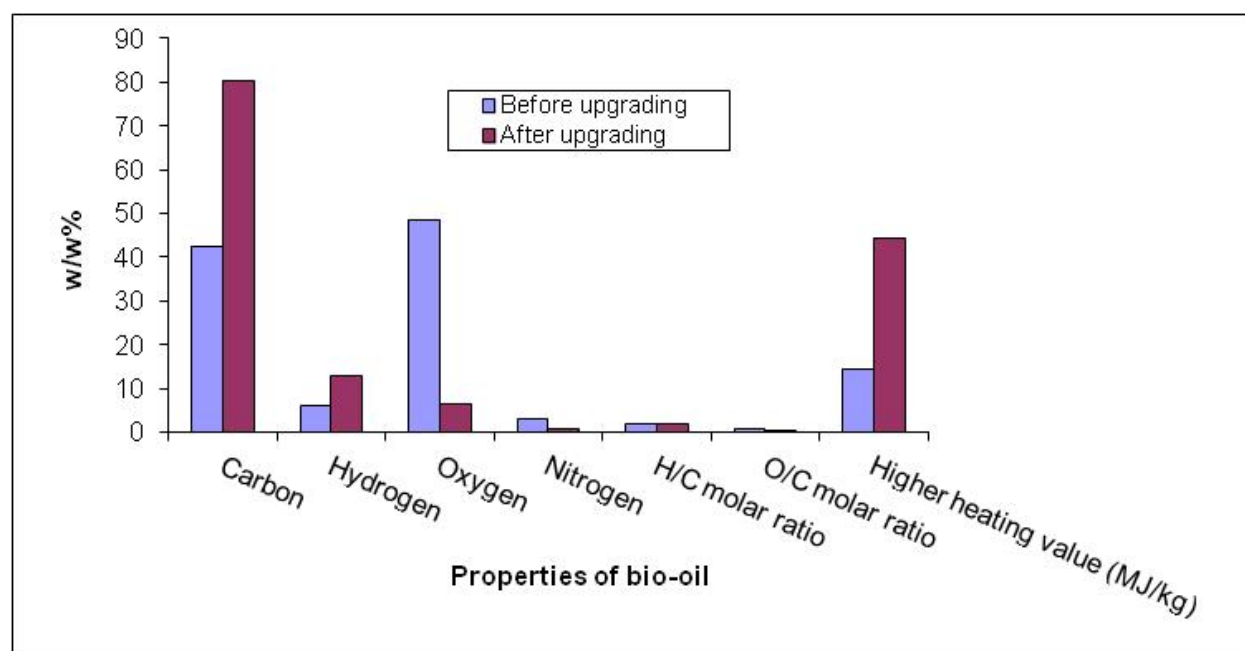

Figure 5. Change of characteristics before and after upgrading bio-oil derived from soybean stalk (Information adapted from Li et al. [8].)

2.2. Reactions involved in deoxygenation

As previously mentioned, deoxygenation involves the removal of functionality of biomass constituents associated with -OH, -COOH, and -C=O. The bond dissociation energies (BDE) for these functional groups are quite high and can be written in descending order as follows:

C-O (1076.5 kJ/mol) > C=O (749 kJ/mol) > C-C (610.0 kJ/mol) > O-H (429.99 kJ/mol) > C-H (338.4 kJ/mol).

Higher BDE for a particular functional group implies that the activation energy required for dissociating this bond (deoxygenation) would also be high. This would dictate rigorous reaction conditions for particularly C-O and C=O bond scissions. The presence of large amount of C=O groups in the pyrolysis products can be related to the higher activation energies required for dissociation of these bonds. However, using appropriate catalysts, these high activation energies could be overcome.

2.2.1. Dehydration

Bio-oil has significant amounts of –OH groups in its components that require dehydration, i.e., removal of oxygen in the form of water, to make hydrocarbons. Dehydration occurs even during HDO process but what is considered here is the spontaneous removal of oxygen as water in the absence of extraneous H_2.

Studies on dehydration as a method to produce motor fuel initiated several decades ago. With the advent of new catalysts, this area grew into new heights. A wide range of studies have been carried out with oxygenates ranging from simple methanol, to polyols like glycerol. The presence of light-molecular-weight alcohols such as methanol and ethanol in bio-oil is less common while phenolic compounds and polyols can be considered to be more abundant. However, studies on light alcohols give good insights into the chemistry and will be discussed in more detail below.

Dehydration of methanol to produce gasoline products such as benzene, toluene and xylene has been reported by different research groups [31-35]. In this regard, different heterogeneous catalysts have been studied. In particular, the molecular sieve ZSM-5 has received great attention for dehydration reactions. It has been widely accepted that Brønsted acid sites of the ZSM-5 catalyst play a crucial role for the dehydration reaction. Acid sites donates protons to the hydroxyl group of the oxygenate as shown in figure (7) to form water instigating dehydration.

Addition of metal oxides onto the catalyst framework was reported to increase the acidity of the support material. As a result, this would enhance dehydration reactions in turn facilitating the formation of higher molecular weight hydrocarbons. For example, methanol conversion to gasoline range hydrocarbons over metal oxides (such as ZnO and CuO) supported on HZSM-5 at temperature 400 °C and 1 atm pressure was reported [36]. The results indicate that pure HZSM-5 produced the lowest yields compared to metal-oxide-promoted catalyst such as CuO/ HZSM-5, CuO /ZnO/HZSM-5, ZnO/HZSM-5. The presence of CuO significantly increased the yields of aromatics. It was further concluded that addition of ZnO over CuO significantly reduced the catalyst deactivation potential [36]. Studies conducted to find the effect of different CuO loadings on methanol conversion indicate that the highest conversion of 97% was obtained when the CuO loading was at 7%. It was observed that further increase of oxide loading decreased methanol conversion. This behavior was attributed to loss of acid sites on the support. A subsequent catalyst deactivation study indicated that the catalyst deactivation increased with the increase in CuO loading. It was concluded that the deactivation of the catalyst occurred mainly due to

the deposition of large molecular weight hydrocarbons known as coke blocking the catalyst pores[37].

Dehydration of ethanol has also been studied extensively with other catalysts. A study of the effect of different additives such as ZnO, Ga_2O_3, Mo_2C and Re, on ZSM-5 on deoxygenation of alcohols has provided new insights on renewable aromatic hydrocarbons production [38]. The product selectivities for different catalysts are depicted in figure (8). It is clear that Ga_2O_3 performed better in terms of selectivity toward benzene, toluene and xylenes found in gasoline.

Figure 6. The two form of acid sites that exist in zeolites.
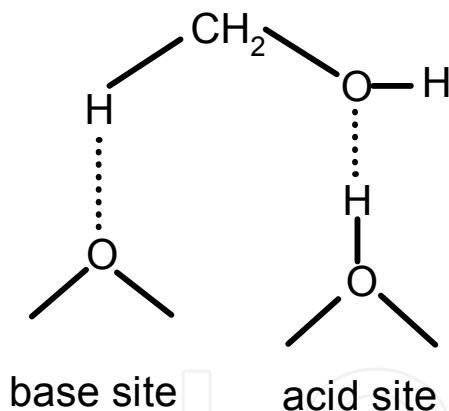

Figure 7. The proposed adsorption of methanol on ZSM-5.(Information was adapted from Chang et al. [31])

Ethanol dehydration has been further studied in order to make ethylene as the precursor to make ethyl-tetra-butyl-ether (ETBE) [39, 40]. Ethers have gained much attention as a substitute for petroleum diesel. A study on ethanol dehydration to ethylene over dealuminated modernite (DM) and metals such as Zn, Mn, Co, Rh, Ni, Fe and Ag loaded DM has shown that Zn/DM and Zn/Ag/DM gives the highest selectivity to ethylene formation [40]. This indicates that incorporation of single metal or metal combinations onto dealuminated modernite makes the catalyst more selective toward ethylene production. Further , the results suggest that such combinations of metal and support would lower coke formation as high molecular weight compounds were not produced significantly.
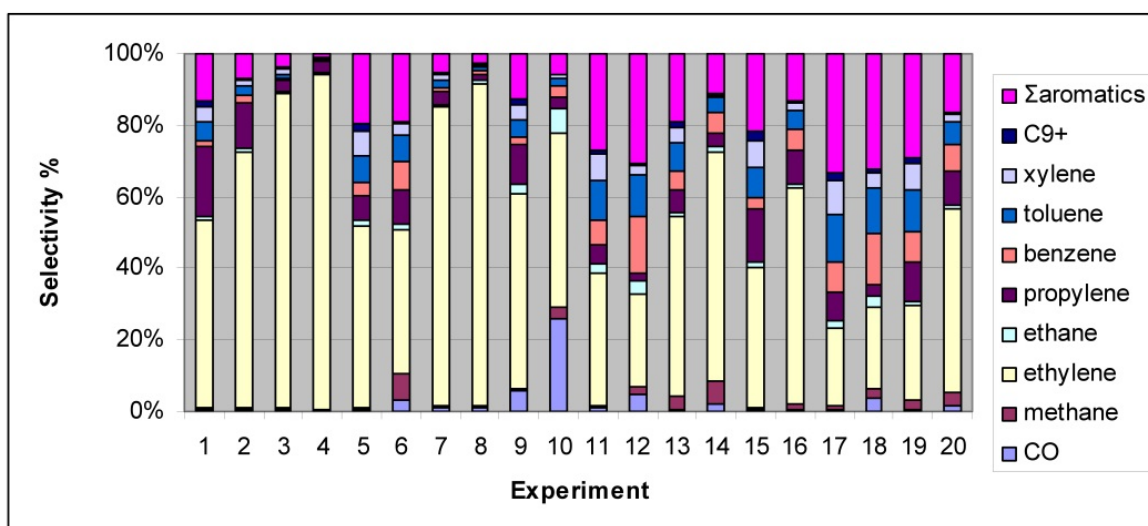
(a)

Experiment No:	Catalyst used	Reaction Temperature -K
1	ZSM-5(80)	773
2	ZSM-5(80)	873
3	ZSM-5(280)	773
4	ZSM-5(280)	873
5	2% Mo$_2$C/ZSM-5(80)	773
6	2% Mo$_2$C/ZSM-5(80)	873
7	2% Mo$_2$C/ZSM-5(280)	773
8	2% Mo$_2$C/ZSM-5(280)	873
9	2% Re/ZSM-5(80)	773
10	2% Re/ZSM-5(80)	873
11	2% Ga$_2$O$_3$/ZSM-5(80)	773
12	2% Ga$_2$O$_3$/ZSM-5(80)	873
13	2% ZnO/ZSM-5(80)	773
14	2% ZnO/ZSM-5(80)	873
15	ZSM-5(80) + 2% Mo$_2$C/ZSM-5(80)	773
16	ZSM-5(80) + 2% Mo$_2$C/ZSM-5(80)	873
17	ZSM-5(80) + 2% Ga$_2$O$_3$/ZSM-5(80)	773
18	ZSM-5(80) + 2% Ga$_2$O$_3$/ZSM-5(80)	873
19	ZSM-5(80) + 2% ZnO/ZSM-5(80)	773
20	ZSM-5(80) + 2% ZnO/ZSM-5(80)	873

(b)

Figure 8. (a) Selectivity towards different products from ethanol dehydration. (b) The catalysts and respective reaction conditions for each reaction.(Prepared with data from Barthos et al.[38])

There has been some studies on phenol dehydration [41, 42]. In once such study where HZSM-5 was used it has been observed that the reactivity of phenol and 2-methoxyphenol has been very low and that the catalyst had a greater tendency to form coke [42]. The rate of deactivation of the catalyst by coke formation reduced with increased water formation. In a separate study, lignin derivative guaiacol was attempted to be transformed to phenol at a temperature of 350 $^{\circ}$C and 1atm pressure. In this study, first row transition metals (V to Zn) supported on alumina was tested [43]. Results indicate that vanadium oxide on alumina

gave the highest yield of phenol. They concluded that vanadium, as an early transition metal, has the oxophilic property and had helped the efficient removal of oxygen from guaiacol in the form of water. Nevertheless, water formed during dehydration has a tendency to adsorb onto acid sites dramatic decreasing the catalyst activity.

2.2.2. Decarboxylation

Bio-oil contains considerable amounts of acids such as acetic, formic, and butyric acid, resulting in low pH values (c.a. pH 2-3). The presence of these acids creates various practical challenges for bio-oil applications. Highly corrosive nature makes bio-oil not suitable for applications with metals and rubber. Further, the presence of acids would increase O/C ratio and make bio-oil more reactive. Accordingly, it is critical to develop chemistries that can deal with carboxylic acids when upgrading bio-oil. Decarboxylation refers to the removal of oxygen in the form of CO_2 from a carboxylated compound and can be given in a general equation as follows (eq.(2)):

$$RCO_2H \rightarrow RH \; + \; CO_2 \tag{2}$$

Insights on effective catalysts for removing oxygen in carboxylic acids can be obtained from studies on decarboxylation of model systems that include stearic, palmetic, benzoic, and heptanoic acids. Equations (3) and (4) depict the thermodynamic favorability of the decarboxylation reactions. The negative values for ΔG^o implies that the decarboxylation reactions of acetic and benzoic acids have a significant activation energy barrier to overcome[44].

$$CH_3CO_2H \rightarrow CH_4 + CO_2 \qquad \Delta G^o = \; -68.5 \, kJ \, / \, mol \tag{3}$$

$$C_6H_5CO_2H \rightarrow C_6H_6 + CO_2 \qquad \Delta G^o = \; -54.3 \, kJ \, / \, mol \tag{4}$$

Biodiesel research is an important area to look for information related to decarboxylation. Fatty acids and fatty acid methyl esters from biodiesel industry have been subjected further deoxygenation with the intension of obtaining higher quality liquid fuels [45, 46]. In one such study, Pd has been identified to be an active metal for decarboxylation of fatty acids present in plant oil. In this study, the ability to convert heptanoic acid to octane was investigated using Pd/SiO2 and Ni/Al2O3 catalysts [47-50]. It was reported that 98% acid conversion was obtained with Pd/SiO2 at 330°C but only 64% was reported by Ni/Al2O3 [44].

Pd supported on active carbon has also been tested as the catalyst for decarboxylation of stearic acid at 300°C. The results indicated that the reaction was selective toward *n*-heptadecane [47]. Further, they claimed that conducting the reaction in the presence of hydrogen increased the rate of decarboxylation. A comparative study performed with thermal and catalytic deoxygenation of stearic acid further proved that catalytic deoxygenation is highly selective toward hydrocarbons. In this study, 5%Pd supported on mesoporous silica, SBA-15, MCM-41and zeolyte-Y has been used as the catalyst. It was reported that SBA-15 had a selectivity of 67% for n-pentadecane [48]. The study further

revealed that the deoxygenation activity reduces in the order as SBA -15 > MCM-41 > zeolite-Y.

In an analogous study, pure palmitic acid, stearic acid, and a mixture of 59% of palmitic and 40% of stearic acid was deoxygenated over 4 % Pd/C catalyst at 300 oC and 5% H2 in argon at 17 bar of pressure. The conversion of the catalyst was reported to be over 94% after 180 min of the reaction time with a selectivity of 99% [51]. The kinetic behavior of decarboxylation of ethyl stearate over Pd / C has been investigated with the aim to verify the reaction mechanism. As shown in figure (9), decarboxylation of ethyl stearate proceeded through fatty acid decarboxylation to the desired *n*-heptadecane. The produced paraffin simultaneously dehydrogenated to unsaturated olefins and aromatics. A kinetic model has been developed based on the proposed reaction network in figure (9) using Langmuir–Hinshelwood mechanism with the assumptions that the surface reaction is rate limiting and the adsorption reaction is rapid compared to surface reaction [52]. The rate equation for the proposed reaction scheme can be represented in a simplified form as shown in eq.(5). According to the rate information, step 6 in figure (9) can be considered as the rate limiting step with the rate constant of 1.45×10^{-12}/min. Both decarboxylation steps which were represented in step 4 and 5 is shown to be the fastest steps in the scheme.

$$r_i = \frac{k_i \bullet C_i}{\left(1 + \sum_i K_i \bullet C_i\right)} \tag{5}$$

(r_i: reaction rate, k_i: lumped reaction rate, C_i: concentration, K_i: equilibrium constant)
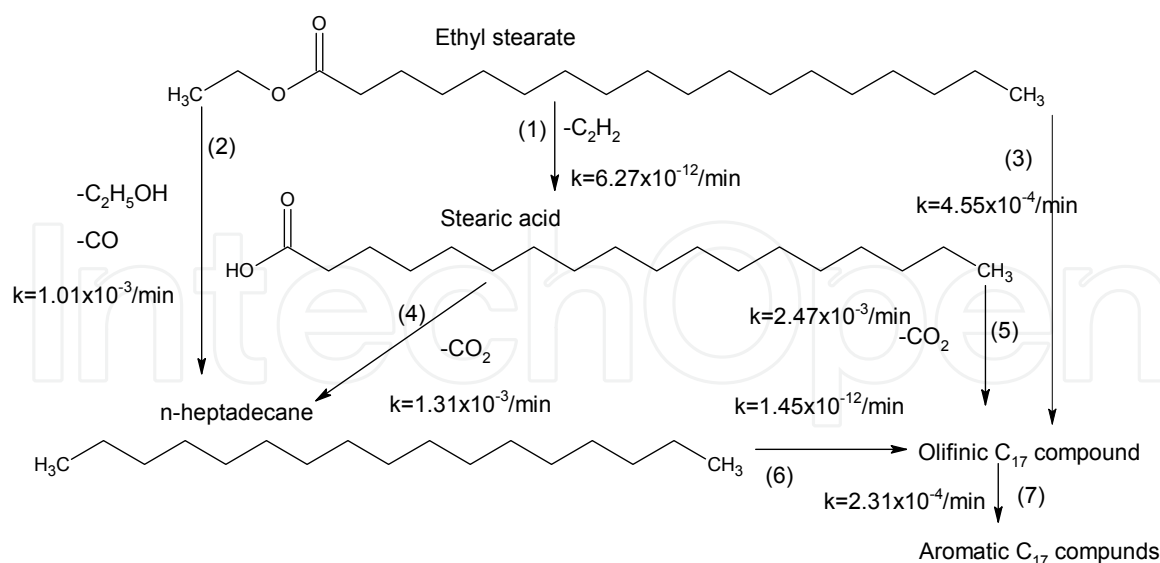

Figure 9. Decarboxylation of elthyl stearate (Information was adapted from Snare et al.[52])

HZSM-5 can be considered as a versatile catalyst that has the ability to do both dehydration and decarboxylation. For example, decarboxylation of methyl esters to hydrocarbon fuels has been studied using methyl octonoate (MO) on HZSM-5 [53]. The catalyst showed strong

signs of MO adsorption on to the catalyst surface. This reaction produced significant amounts of C1-C7 hydrocarbon compounds and aromatics. Formation of octonic acid as a primary product indicates that acidic hydrolysis reaction has taken place. However, it was noted that these primary products further undergo conversion into aromatic compounds. The proposed reaction scheme for the MO conversion is presented in figure (10).
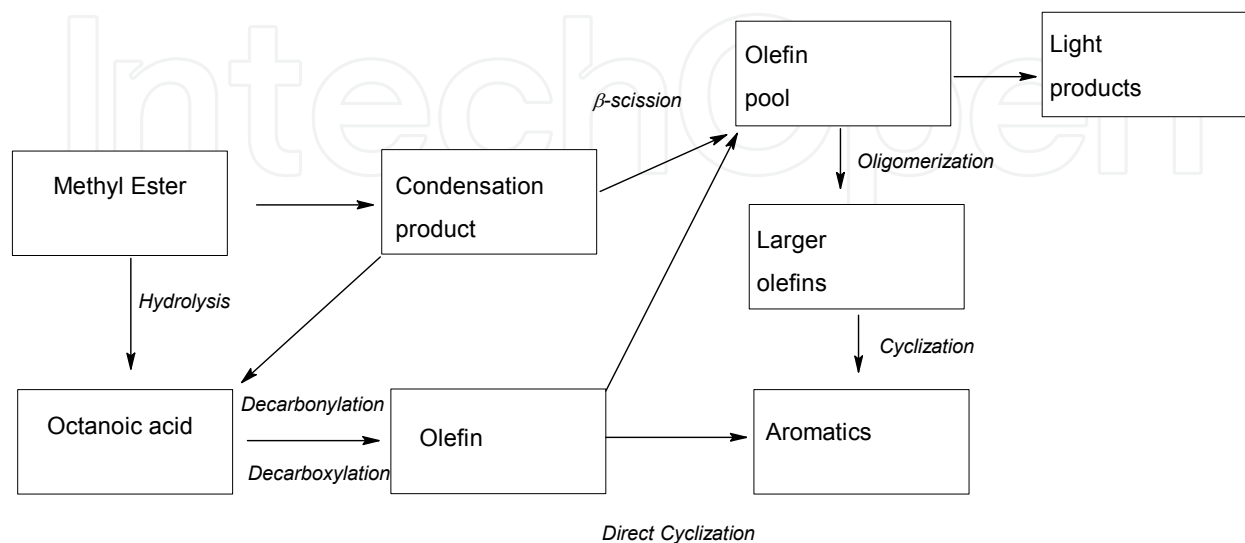

Figure 10. A possible reaction pathway for the deoxygenation of methyl octonoate (Information was adapted from Danuthai et al. [53]).

Rather than complete removal, partial removal of oxygen to aldehydes or ketones would also be useful during upgrading since the latter product(s) can go through HDO pathway relatively easily. Various studies have been conducted in this regard and many have used benzoic acid as the model compound [54-58]. In such a study, different weak base catalysts such as MnO_2, CeO_2, MgO, ZnO, Fe_2O_3, K_2O supported on SiO_2, Al_2O_3, TiO_2 have been tested for upgrading the acid-rich phase of bio-oil through ketonic condensation. The study further evaluated the effect of the presence of water on ketonic condensation of three model components, phenol, p-methoxyphenol, and furfural (typically seen in bio-oil). They reported that CeO_2 on Al_2O_3 and TiO_2 had better catalytic activity and tolerance to water. Although the presence of water and phenol did not have a significant impact on the ketonic condensation of acetic acid, the presence of furfural exhibited a strong inhibitory effect on the reaction [54].

Recent studies reported that the best catalysts for the conversion of carboxylic acids to aldehyde /alcohol(s) were Al_2O_3, SiO_2, TiO_2 or MgO supported transition/noble metals such as Pt, Pd, Cu, or Ru. For example, in deoxygenation of methyl stearate and methyl octanoate over alumina-supported Pt [59], 1% Pt/γ-Al_2O_3 reported to be highly active and selective toward deoxygenation. They reported that 1% Pt/TiO_2 displayed a higher C_8 hydrocarbon selectivity than 1% Pt/Al_2O_3. This was attributed to the presence of larger oxygen vacancies on the TiO_2 support [59]. Results of a similar screening study for the decarboxylation of stearic acid are depicted in the figure (11). It is apparent that Pd, Pt on activated carbon and 5% Ru on MgO resulted in the highest conversion of stearic acids to hydrocarbons.
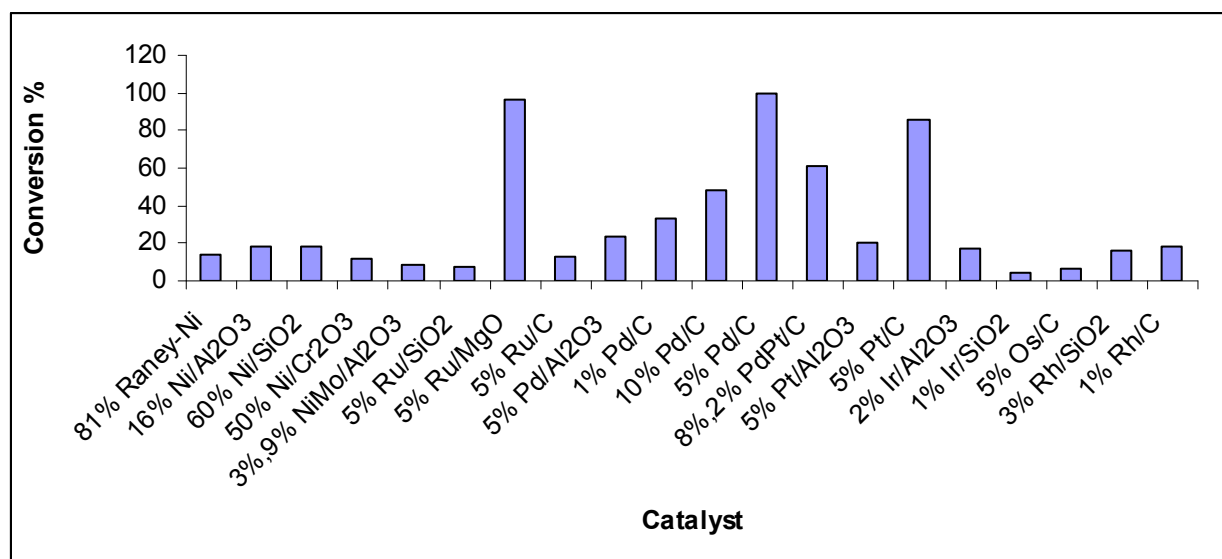
Figure 11. Conversion of stearic acid on different catalysts (Information was adapted from Snare et al. [45].)

2.2.3. Decarbonylation

In general, bio-oil contains significant amounts of aldehydes and ketones c.a. 10.9% and 36.6% respectively. The presence of carbonyl groups in the structure reduces the heating value and stability of bio-oil. Therefore, selective removal of carbonyl group as carbon monoxide as given in eq. (6) is another route to make bio-oil a more favorable fuel intermediate. However, the level of understanding of decarbonylation as a route for the upgrading bio-oil is still quite limited.

$$RCOH \rightarrow RH \ + \ CO \qquad (6)$$
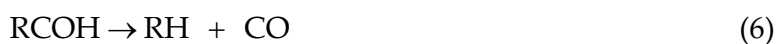
According to literature, decarbonylation and decarboxylation are integral reactions in the deoxygenation of carboxylic acids and esters. At times, instead of removing CO_2, removal of CO and H_2O can take place in the deoxygenation step and is considered as decarbonylation. Moreover, product(s) derived by decarbonylation / decarboxylation are not significantly different from those obtained from hydrogenolysis [47].

Decarbonylation usually takes place over supported noble metal catalysts such as Pd/C at elevated temperatures [47]. A study on decarbonylation reaction has been carried out to understand the effect of the presence of Cs on zeolyte-X for the deoxygenation of methyl octanoate (MO) as well as the effect of methanol co-feeding with MO [60]. The results indicated that the decarbonylation of MO occurs at a higher rate and for extended periods over CsNaX when co-fed with methanol. The surface analysis revealed that MO strongly adsorbed on basic sites of CsNaX and Cs improved the basicity of the catalyst. It was concluded that not only the basicity of the catalyst but also the polar nature of the zeolite catalyst assisted the decarbonylation process [60].

Deoxygenation of aldehyde, ketone and carboxylic acid containing bio-oil constituents has been studied using model compounds such as acetaldehyde, acetone, butanone, and acetic

acid [61]. In this study, HZSM-5 was used as the catalyst. Acetone was considered to undergo a reaction via a mechanism as depicted in figure (12). The results indicated that acetone is less reactive than alcohols and that a higher space velocity was needed to achieve higher conversion into aromatics. A significant increase in coke formation had been observed for both aldehyde and carboxylic acids compared to alcohol.

The ongoing interest in understanding decarbonylation mechanism(s) under the umbrella of organometalic chemistry has resulted in some useful insights. For example, a theoretical and an isotope labeled experimental study of decarbonylation of benzaldehyde and phenyl acetaldehyde on rhodium surface in the presence of bidentate phosphine ligand indicate that decarbonylation mechanism consists of oxidative addition, migratory extrusion, and reductive elimination with migratory extrusion as the rate-determining step [62].
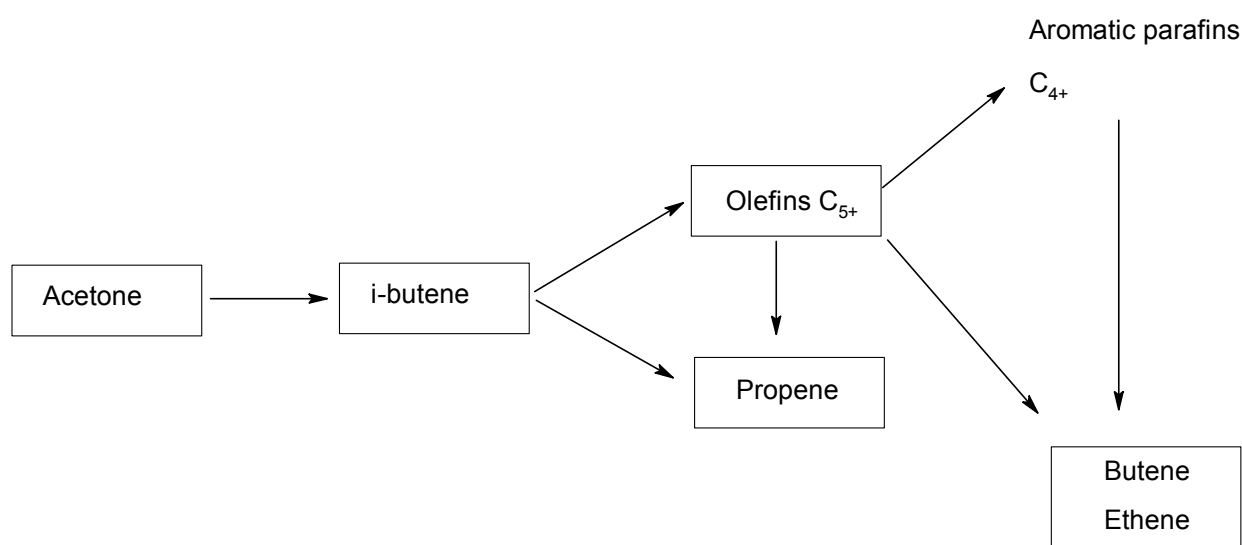
Figure 12. The reaction scheme for acetone decarbonylation on HZSM-5 (In formation was extracted from Gayubo et al. [61].)

Using DFT calculations, it has been deduced that decarbonylation of acetaldehyde is assisted by Co^+ as the representative transition metal ion. The study concludes that decarbonylation of acetaldehyde follows four steps, i.e., complexation, C–C activation, aldehyde H-shift and nonreactive dissociation [63].

Furan, C_4H_4O is one of the common oxygenated compounds in the biomass derived bio-oils that has been used to study decarbonylation. Adsorption and desorption steps of furan on pure metal surfaces during the deoxygenation reaction can be found in many publications [64-66]. Some studies on furan decarbonylation has been conducted on different single crystal metal surfaces such as Cu (110), Ag (110) and Pd(111). It was observed that furan absorbs on Cu, Ag and, under mild temperatures, on Pd. Under mild conditions, it was observed that furan desorbs on the metal surface without disrupting the molecule, but, at elevated temperatures, undergoes a deoxygenation reaction [67].

3. Upgrading techniques for fuel production

In any biomass to biofuels conversion process, above mentioned three reaction pathways can be considered to be quite significant. Depending on the process conditions such as temperature, pressure, the resident time and the type of catalyst, the degree to which these reactions would take place may vary. Basically the major processes that are exploited during deoxygenation pathways are secondary cracking, fast catalytic cracking and hydrodeoxygenation.

3.1. Secondary pyrolysis

This is the simplest process with no catalyst involved for the deoxygenation of biomass oxygenates and occurs with fairly low efficiencies. The concept behind this process is simply to route the pyrolysis vapor through a second reactor which is maintained at a high temperature. The thermal cracking reaction initiated in the secondary reactor would remove oxygen as H_2O, CO_2 and CO. Due to the thermodynamic nature of this reaction, increased resident times would favor formation of thermodynamically more stable species such as CO_2 and CO. The significant drawback of this method is the higher tendency of losing carbon in the forms of CO_2 and CO.

3.2. Catalytic upgrading

Catalytic upgrading process is conducted in a number of different ways. Most commonly practiced method would be injection of bio-oil into a tubular reactor packed with a catalyst capable of deoxygenating the substrates. Due to the inefficacies associated with condensing and reheating processes, a reactor capable of accepting a direct feed of pyrolysis vapor into its catalytic chamber has become more popular. Numerous forms of Zeolites are known to be effective for deoxygenation[68] of which ZSM-5 is widely touted to be the most effective catalyst for deoxygenation (via decarboxylation, decarbonylation or dehydration pathways). ZSM-5 is a molecular sieve with 5.5 Å pore channels. This pore structure is responsible for the high selectivity of ZSM-5 toward aromatic hydrocarbons. Deoxygenation reaction on ZSM-5 is believed to be catalyzed at the Bronsted acid sites and its structure is depicted in fig.6.

3.3. Hydrodeoxygenation (HDO)

Due to the hydrogen deficient nature of biomass (C:H<1), catalytic upgrading of bio-oil often leads to deoxygenation via decarboxylation and/or decarbonylation routes leading to losing of precious carbon assimilated during photosynthesis. Analogously, dehydration, in a hydrogen-lean environment leads to formation of large unsaturated compounds commonly known as coke. In order to circumvent these issues, extra hydrogen is supplied to the reactor - and this process is called hydrodeoxygenation.

So far the most reliable and extensively studied method for deep deoxygenation is hydrodeoxygenation which involves gaseous hydrogen and heterogeneous catalyst such as

sulfided NiMo, CoMo supported on alumina[69] [70].The idea of using hydrogen to upgrade bio-oil originates from the use of hydrogen in the petrochemical industry. Hydroprocessing is a crucial step in petroleum refining process that basically involves five types of reaction classes: hydrodenitrogenation (HDN), hydrodesulfurization (HDS), hydrodeoxygenation (HDO), hydrodemthylation (HDM) and hydrogenation (HYD)[70-72].

The process where oxygen in the feed is removed via dehydration using gaseous hydrogen is called hydrodeoxygenation (HDO). In a typical hydro processing process, the order of these reaction classes are HDS>HDO>HDN. This is because in a conventional petroleum feed, the sulfur and nitrogen content is significantly higher compared to oxygen. Therefore, HDO chemistry has received only little attention in petrochemical refining [27]. Hydrotreatment of crude petroleum is challenging for the catalyst due to the presence of sulfur and nitrogen in the feed in significant amounts. The products of hydrotreatment such as water, ammonia, hydrogen sulfide has been reported to poison hydrotreating catalysts [73]. Nevertheless, since bio-oil contains less sulfur and nitrogen, HDO would be a better fit for bio-oil upgrading. The presence of significant amounts of oxygen and C=C compounds in bio-oil increases chances of simultaneous occurrence of HDO as well as the hydrogenation reactions. More negative Gibbs free energies of deoxygenation reactions compared to hydrogenation reactions implies that deoxygenation is more favorable. However, saturation of aromatic rings is not desirable as it consumes large amounts of hydrogen and reduces the octane number of the fuel reducing the fuel quality.

Much of the studies on HDO are based on catalysts such as Co-Mo, Ni-Mo, Ni-W, Ni, Co, and Pd. A catalyst, to be effective for HDO, should ideally perform two tasks, i.e., activating the dihydrogen molecule as well as activating the oxygen group of the compound. The oxygen group activation usually occurs on the transition metal oxides such as Mo, W, Co, Mn, Zr, Ce, Y, Sr and La while the activation of hydrogen is known to happen on noble metals such as Pt, Pd, and Rh [74].

Studies on HDO chemistry has mostly been done using model compound such as phenol, cresole, guaiacol, napthol etc. [75, 76] which are abundantly present in bio-oil. Some of these model compounds and their proposed reaction pathways are shown in Table (2).

Most of the earlier work in HDO used sulfided forms of Mo as the active element and Co or Ni as promoters on $\gamma.Al_2O_3$ [27, 70, 79]. However, sulfide catalyst would not work for bio-oil since the feed does not contain significant amounts of sulfur. In the HDO process, a sulfide catalyst would soon be deactivated if an external sulfur source is not provided [80]. Nevertheless, the oxygen content of the feed is said to have a negative effect on the sulphide structure resulting in losses such as the catalyst deactivation and changes in product distribution. In-depth studies on Co (or Ni)-promoted MoS_2 catalysts have revealed that the edges on MoS_2 is also important in terms of catalyst activity since they are dominated by promoter atoms in the so-called Co–Mo–S structures [81]. The studies have revealed that poly-condensation products formed have shortened the life by deactivation. Alumina in this regard is quite susceptible to deactivation by coke formation. Therefore, investigations on new catalysts that do not require sulfidation and supports such as activated carbon that are tolerant to deactivation are needed[82].
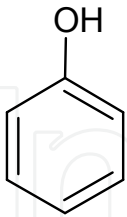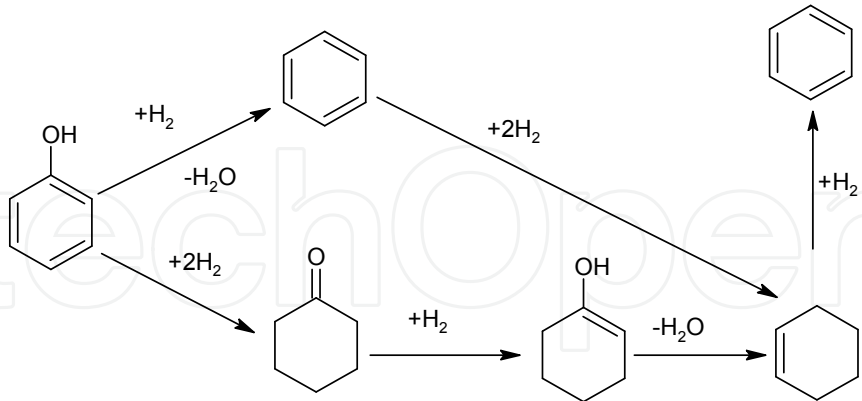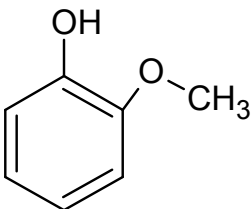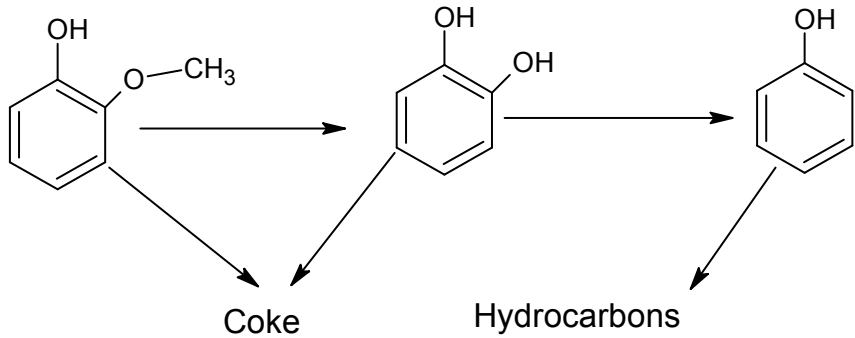
Oxygenate compound	Proposed hydro-deoxygenation reaction	Ref.
Phenol		[77]
Guaicol		[78]

Table 2. Common reaction pathways proposed for HDO reactions. (Reaction schemes were extracted from Senol et al [77]and Laurent et al.[78])

The suitability of Ni as a catalyst to activate the dihydrogen molecule in HDO has been reported by several groups[79, 83]. In comparison to noble metals, the use of Ni is extremely economical especially for large scale applications. For example, the gas-phase hydrodeoxygenation of a series of aromatic alcohols that include aldehydes and acids has been reported with Ni/SiO_2. This study analyzed kinetic effects of the gas phase hydrogenolysis of $-CH_2OH$, $-CHO$ and $-COOH$ groups attached on to aromatic ring structures in the presence of Ni/SiO_2 [79]. They concluded that the oxygenated aromatics get weakly adsorbed on the catalyst and the surface mobility facilitates reaction with adsorbed hydrogen atoms. Further, the adsorption reactions of H_2 and aromatic species were considered to be a competitive adsorption.

In a separate study, HDO of model compound anisole using Ni-Cu on Al_2O_3, CeO_2 and ZrO_2 supports found that Ni–Cu supported on CeO_2 and Al_2O_3 was the most active catalyst in comparison to pure Ni catalyst[74]. The significance of this study was that the catalysts

tested were not in the sulfided form and therefore would be highly suitable for bio-oil-type application(s).

The need for hydrogen in HDO process has always been a point of concern due to high expenses associated with hydrogenations. A study in this regard attempted using hydrogen generated in situ for performing HDO. A study conducted using Pt on TiO_2, CeO_2, and ZrO_2 supports showed that the oxygenates undergo dehydrogenation and subsequently HDO using the produced H_2. The catalysts tested were Pt/CeO_2, $Pt/CeZrO_2$, Pt/TiO_2, Pt/ZrO_2, $Pt/SiO_2-Al_2O_3$, and Pt/Al_2O_3. Of all catalysts tested, Pt on Al_2O_3 showed the highest activity with a reduction of oxygen content from 41.4 wt% to 2.8 wt% after upgrading [84].

It has also been shown that Pd on supports such as carbon, Al_2O_3, ZSM-5, MCM 41 [76, 85, 86] are active for HDO. A study conducted with benzophenone with 5% Pd on active carbon and on ZSM-5 supports proved to be very active toward hydrogenation as opposed to supports such as Al_2O_3, and MCM 41. However, the HDO of benzophenone was significantly higher with Pd on supports like active carbon and acid zeolytes. Furthermore, it was concluded that the acidity of the zeolite support affects the HDO reaction [76].

Co processing of bio-oil with straight run gas oil (SRGO) can be considered to have more practical significance. The concept behind this method is the simultaneous use of HDS process with the HDO of biocrude [69, 87-89]. The model compound guaiacol (5000 ppm) representing oxygenates in bio-oil has been used together with SRGO (containing13,500 ppm of S) in a trickle bed reactor. At low temperature and low space velocities, a decrease in the HDS reaction has been observed with $CoMo/Al_2O_3$. The possible explanation is the competition of intermediate phenol with the sulfur containing molecules for adsorption on hydrogenation/ hydrogenolysis sites. At higher temperatures (above 380^{0}C), the HDO of guaiacol was observed along with HDS taken place without further inhibition [88] .

Although the role of sulfur on HDS is well understood, the effect of sulfur on HDO is not yet well explained. Certain studies indicate that the presence of H_2S has an inhibitory effect on the HDO while other studies support maintaining the sulfidasation level of the catalyst [90-92]. For example, the effect of using a sulfiding agent, H_2S has been studied with model compounds like phenol and anisole during hydrotreatment. The results conclude that the presence of H_2S decreases the HDO activity of the sulfided $CoMo/\gamma-Al_2O_3$ catalyst and the product yield depends on the concentration of H_2S [80]. A similar study conducted using H_2S for HDO of phenol on Co-Mo and Ni-Mo arrived at the same conclusion. However, quite interestingly, the presence of H_2S during the HDO of aliphatic oxygenates has shown a promoting effect. The reason for this observation is that the sulfiding agent , H_2S, enhances the acid catalyzed reactions of aliphatic oxygenates. However, direct hydrogenolysis reaction of phenol is suppressed due to competitive adsorption of both phenol and H_2S [77, 93].

4. Concluding remarks

During pyrolysis or liquefaction, biomass undergoes a series of complex conversion processes producing bio-oil. Bio-oils are highly diverse in its composition and has a

spectrum of oxygenates. Due to the presence of a collective of different oxygenated compounds, an upgrading process to remove oxygen would likely involve a series of reactions. This review introduces several possibilities for upgrading bio-oil including dehydration, decarboxylation and decarbonylation. A summary of the best catalyst contenders for each reaction class is given in the Table 3.

Reaction class	Reaction details	Catalyst	Best performance
Dehydration	Methanolconversion to gasoline range products	HZSM-5, ZnO/HZSM-5, CuO/HZSM-5	CuO/HZSM-5 (7% loading of CuO is said to be best)
	Ehtanol conversion to hydrocarbon	HZSM-5 ZnO/ ZSM-5 Ga_2O_3/ZSM-5 Mo_2C/ ZSM-5 Re/ ZSM-5	Ga_2O_3/ZSM-5
	Ehtanol to ethylene	dealuminated modernite (DM) Zn/DM Mn/DM Co/DM Rh/DM Ni/DM Fe/ DM Ag/DM	Zn on dealuminated modernite
Decarboxylation	Conversion of heptanoic acid to octane	Pd/SiO_2 Ni/Al_2O_3	Pd/SiO_2
	Deoxygenation of stearic acid	5%Pd supported on messoporous silica - SBA15, -MCM41 zeolyte-Y	5%Pd -SBA15
	Ketonic condensation of acetic acid	MnO_2, CeO_2, MgO, ZnO, Fe_2O_3, K_2O supported on SiO_2, Al_2O_3, TiO_2	CeO_2 supported on Al_2O_3, or on TiO_2
Decarbonylation	Deoxygenation of methyl octanoate	Cs on NaX zeolyte	Cs on NaX zeolyte
	Deoxygenation of acetaldehyde, acetone, butanone, and acetic acid	HZSM-5	HZSM-5

Table 3. Summary of best performing catalyst for each reaction class.

Hydrodeoxygenation has been the most frequently studied and one of the most reliable methods that could be used for deoxygenation of oxygenates. However, the drawbacks of hydrodeoxygenation include: the need for continuous replenishment of sulfur (for sulfided catalysts), and the non-selective deoxygenation of all bio-oil chemical moieties resulting in a spectrum of short-chained and long-chained hydrocarbons that are less useful as liquid fuels. The need of hydrogen makes resulting biofuels less competitive with existing petroleum fuels. More research is needed on development of effective non-sulfided hydrodeoxygenation catalysts. Preliminary investigations with Ni-Cu on CeO_2 or ZrO_2 may provide new directions on this front. Further research should be directed on identifying materials and processes will allay the need for using direct hydrogen.

According to the analysis, metal promoted or unpromoted HZSM-5 proves to be one of the most versatile catalysts that is capable of catalyzing all three deoxygenation reaction classes, i.e., dehydration, decarboxylation and decarbonylation. Nevertheless, the nanopore structure of HZSM-5 (~5.4-5.5 Å), while assisting size selectivity for gasoline range hydrocarbons, also promotes pore blockages resulting in rapid catalyst deactivation. Developing catalysts of the same class, with larger and consistent pore structure and/or higher activity/functionality should be closely looked at.

Author details

Duminda A. Gunawardena and Sandun D. Fernando
Department of Biological and Agricultural Engineering, Texas A&M University, College Station, Texas, USA

5. References

[1] Demirbas, A., Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. Energy Conversion and Management 2008. 49: p. 2106–2116.

[2] Demirbas, M.F. and M. Balat, Recent advances on the production and utilization trends of bio-fuels: A global perspective. Energy Conversion and Management 2006. 47: p. 2371–2381.

[3] Bridgwater, A.V., D. Meier, and D. Radlein, An overview of fast pyrolysis of biomass. Organic Geochemistry 1999. 30: p. 1479-1493.

[4] Bhattacharya, S.C., et al., Sustainable biomass production for energy in selected Asian countries. Biomass and Bioenergy 2003. 25(5): p. 471 – 482.

[5] Perlack, R.D., et al., Biomass as a feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion-ton annual supply., O.R.N. Laboratory, Editor 2005, U.S. Department of Energy U.S. Department of Agriculture.

[6] Association, I.E., Key World Energy Statistics 2011, 2011: Paris.

[7] Hayes, D.J., An examination of biorefining processes, catalysts and challenges. Catalysis Today, 2009. 145 (1-2): p. 138-153.

[8] Li, J., L. Wu, and Z. Yang, Analysis and upgrading of bio-petroleum from biomass by direct deoxy-liquefaction. Journal of Analytical and Applied Pyrolysis, 2008. 81(2): p. 199–204.

[9] Reed, T.B. and A. Das, Handbook of Biomass Downdraft Gasifier Engine System, 1988, Solar Energy Research Institue: Golden, Colorado.

[10] Klerk, A.d., Hydroprocessing peculiarities of Fischer-Tropsch syncrude. Catalysis Today, 2008. 130(2-4): p. 439.

[11] Maitlis, P.M., Fischer–Tropsch, organometallics, and other friends. Journal of Organometallic Chemistry 2004. 689: p. 4366–4374.

[12] Lamprecht, D., Hydrogenation of Fischer-Tropsch Synthetic Crude. Energy & Fuels, 2007. 21(5): p. 2509-2513.

[13] Henstra, A.M., et al., Microbiology of synthesis gas fermentation for biofuel production. Current Opinion in Biotechnology, 2007. 18(3): p. 200-206.

[14] Kleinert, M., J.R. Gasson, and T. Barth, Optimizing solvolysis conditions for integrated depolymerisation and hydrodeoxygenation of lignin to produce liquid biofuel. Journal of Analytical and Applied Pyrolysis, 2009. 85: p. 108–117.

[15] Li, H., et al., Liquefaction of rice straw in sub- and supercritical 1,4-dioxane–water mixture. Fuel Processing Technology 2009. 90: p. 657–663.

[16] Mullaney, H., et al., Technical, Environmental and Economic Feasibility of Bio-Oil in New Hampshire's North Country, 2002, University of New Hampshire.

[17] Zhang, Q., et al., Upgrading Bio-oil over Different Solid Catalysts. Energy & Fuels, 2006. 20(6): p. 2717-2720.

[18] Senneca, O., Kinetics of pyrolysis, combustion and gasification of three biomass fuels. Fuel Processing Technology 2007. 88: p. 87–97.

[19] Shafizadeh, F., Introduction to Pyrolysis of biomass. Journal of Analytical and Applied Pyrolysis,, 1982. 3: p. 283-305.

[20] Lin, Y.-C., et al., Kinetics and Mechanism of Cellulose Pyrolysis. The Journal of Physical Chemistry C, 2009. 113(46): p. 20097-20107.

[21] Bridgwater, T., Applications for Utilisation of Liquids Produced by Fast Pyrolysis of Biomass. Biomass and Bioenergy, 2007. 31(8): p. I-VII.

[22] Fernando, S., et al., Biorefineries:Current Status, Challenges, and Future Direction. Energy & Fuels, 2006. 20(4): p. 1727-1737.

[23] Adjaye, J.D. and N.N. Bakhshi, Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts. Fuel Processing Technology 1995. 45: p. 161-183.

[24] Bridgwater, T., Biomass for energy. Journal of the Science of Food and Agriculture, 2006. 86(12): p. 1755-1768.

[25] Hoekstra, E., et al., Fast Pyrolysis of Biomass in a Fluidized Bed Reactor: In Situ Filtering of the Vapors. Industrial & Engineering Chemistry Research, 2009. 48: p. 4744–4756.

[26] Bridgwater, A.V., Production of high grade fuels and chemicals from catalytic pyrolysis of biomass. Catalysis Today, 1996. 29(1-4): p. 285.

[27] Elliott, D.C., Historical Developments in Hydroprocessing Bio-oils. Energy & Fuels 2007. 3(21): p. 1792-1815.

[28] Huber, G.W. and A. Corma, Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass. Angewandte Chemie Int. Ed. , 2007. 46(38): p. 7184 – 7201.

[29] Radovanovic, M., et al., Some remarks on the viscosity measurement of pyrolysis liquids. Biomass and Bioenergy 2000. 18: p. 209-222.

[30] Qi, Z., et al., Review of biomass pyrolysis oil properties and upgrading research. Energy Conversion and Management 2007. 48: p. 87–92.

[31] Chang, C.D. and A.J. Silvestri, The Conversion of Methanol and Other O-Compounds to Hydrocarbons over Zeolite Catalysts. Journal of catalysis 1977. 47: p. 249-259.

[32] Dass, D.V. and A.L. Odell, A comparative study of the conversion of ethanol and of ethylene over the "Mobil" zeolite catalyst, H-ZSM-5. An application of the Benzene Sequestration Test. Canadian journal of chemistry, 1989. 67: p. 1732-1734.

[33] Barthos, R., et al., Aromatization of methanol and methylation of benzene over Mo2C/ZSM-5 catalysts. Journal of Catalysis 2007. 247(368-378).

[34] Barrett, P.A., et al., Rational design of a solid acid catalyst for the conversion of methanol to light alkenes: synthesis, structure and performance of DAF-4. Chemical communication, 1996: p. 2001-2002.

[35] Chang, C.D., W.H. Lang, and R.L. Smith, The Conversion of Methanol and Other O-Compounds to Hydrocarbons over Zeolite Catalysts II. Pressure Effects. Journal of Catalysis, 1979. 56: p. 169-173.

[36] Zaidi, H.A. and K.K. Pant, Catalytic conversion of methanol to gasoline range hydrocarbons Catalysis Today, 2004. 96(3): p. 155-160.

[37] Zaidi, H.A. and K.K. Pant, Transformation of Methanol to Gasoline Range Hydrocarbons Using HZSM-5 Catalysts Impregnated with Copper Oxide. Korean Journal of Chemical Engineering, 2005. 22(3): p. 353-357.

[38] Barthos, R., A. Sze´chenyi, and F. Solymosi, Decomposition and Aromatization of Ethanol on ZSM-Based Catalysts. Journal of Physical Chemistry- B 2006. 110: p. 21816-21825.

[39] Phillips, C.B. and R. Datta, Production of Ethylene from Hydrous Ethanol on H-ZSM-5 under Mild Conditions. Industrial Engineering Chemmical Reservs 1997. 36: p. 4466-4475.

[40] Arenamnarta, S. and W. Trakarnprukb, Ethanol Conversion to Ethylene Using Metal-Mordenite Catalysts. International Journal of Applied Science and Engineering, 2006. 4(1): p. 21-32.

[41] Sajiki, H., et al., Pd/C-Catalyzed Deoxygenation of Phenol Derivatives Using Mg Metal and MeOH in the Presence of NH4OAc. Organic Letters 2006. 8(5): p. 987-990.

[42] Gayubo, A.G., et al., Transformation of Oxygenate Components of Biomass Pyrolysis Oil on a HZSM-5 Zeolite. I. Alcohols and Phenols. Industrial & Engineering Chemistry Research, 2004. 43: p. 2610-2618.

[43] Filley, J. and C. Roth, Vanadium catalyzed guaiacol deoxygenation. Journal of Molecular Catalysis A: Chemical 1999. 139: p. 245-252.

[44] Maier, W., et al., Gas phase decarboxylation of carboxylic acids. Chemische Berichte 1982. 115(2): p. 808-812.

[45] Snare, M., et al., Heterogeneous Catalytic Deoxygenation of Stearic Acid for Production of Biodiesel. Industrial & Engineering Chemistry Research, 2006. 45: p. 5708-5715.

[46] Kubickova, I., et al., Hydrocarbons for diesel fuel via decarboxylation of vegetable oils. Catalysis Today, 2005. 106 p. 197–200.

[47] Arvela, P.M., et al., Catalytic Deoxygenation of Fatty Acids and Their Derivatives. Energy & Fuels 2007. 21: p. 30-40.

[48] Lestari, S., J. Beltramini, and G.Q.M. Lu. Catalytic deoxygenation of stearic acid over palladium supported on acid modified mesoporous silica. in Zeolites and Related Materials: Trends, Targets and Challenges Proceedings of 4th International FEZA Conference. 2008.

[49] Snare, M., et al., Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons. Fuel 2008. 87: p. 933–945.

[50] Simakova, I., et al., Deoxygenation of palmitic and stearic acid over supported Pd catalysts: Effect of metal dispersion. Applied Catalysis A: General, 2009. 355 p. 100-108.

[51] Lestari, S., et al., Catalytic Deoxygenation of Stearic Acid and Palmitic Acid in Semibatch Mode. Catalytic Letters, 2009. 130: p. 48-51.

[52] Snare, M., et al., Production of diesel fuel from renewable feeds: Kinetics of ethyl stearate decarboxylation. Chemical Engineering Journal 2007. 134: p. 29–34.

[53] Danuthai, T., et al., Conversion of methylesters to hydrocarbons over an H-ZSM5 zeolite catalyst. Applied Catalysis A: General 2009. 361: p. 99–105.

[54] Deng, L., Y. Fu, and Q.-X. Guo, Upgraded Acidic Components of Bio-oil through Catalytic Ketonic Condensation. Energy Fuels, 2009. 23(1): p. 564-568.

[55] Sakata, Y., C.A.v. Tol-Koutstaal, and V. Ponecz, Selectivity Problems in the Catalytic Deoxygenation of Benzoic Acid. Journal of Catalysis 1997. 169: p. 13–21.

[56] Sakata, Y. and V. Ponec, Reduction of benzoic acid on CeO_2 and, the effect of additives. Applied Catalysis A: General 1998. 166 p. 173-184.

[57] Lange, M.W.d., J.G.v. Ommen, and L. Lefferts, Deoxygenation of benzoic acid on metal oxides 2. Formation of byproducts. Applied Catalysis A: General 2002. 231 p. 17–26.

[58] Dury, F. and E.M. Gaigneaux, The deoxygenation of benzoic acid as a probe reaction to determine the impact of superficial oxygen vacancies (isolated or twin) on the oxidation performances of Mo-based oxide catalysts. Catalysis Today, 2006. 117(1-3): p. 46.

[59] Do, P.T., et al., Catalytic Deoxygenation of Methyl-Octanoate and Methyl-Stearate on Pt/Al2O3. Catalysis Letters, 2009.

[60] Sooknoi, T., et al., Deoxygenation of methylesters over CsNaX. Journal of Catalysis 2008. 258: p. 199-209.

[61] Gayubo, A.G., et al., Transformation of Oxygenate Components of Biomass Pyrolysis Oil on a HZSM-5 Zeolite. II. Aldehydes, Ketones, and Acids. Industrial & Engineering Chemistry Research, 2004. 43(11): p. 2619-2626.

[62] Fristrup, P., et al., The Mechanism for the Rhodium-Catalyzed Decarbonylation of Aldehydes: A Combined Experimental and Theoretical. J. AM. CHEM. SOC. 2008, 130, , 2008. 130(45): p. 5206–5215.

[63] Zhao, L., et al., Does the Co+-assisted decarbonylation of acetaldehyde occur via C–C or C–H activation? A theoretical investigation using density functional theory. Chemical Physics Letters 2005. 414: p. 28–33.

[64] Caldwell, T.E. and D.P. Land, J. Phys. Chem. B 1999. 103: p. 7869.

[65] Caldwell, T.E., I.M. Abdelrehim, and D.P. Land, Furan Decomposes on Pd(111) at 300 K To Form H and CO plus C3H3, Which Can Dimerize to Benzene at 350 K. J. Am. Chem. Soc. , 1996. 118(4): p. 907-908.

[66] Ormerod, R.M., et al., Chemisorption and reactivity of furan on Pd{111} Surface Science, 1996. 360(1-3): p. 1-9.

[67] Knight, M.J., et al., The adsorption structure of furan on Pd(111). Surface Science 2008. 602(14): p. 2524–2531.

[68] Putun, E., B.B. Uzun, and A.E. Putun, Rapid Pyrolysis of Olive Residue. 2. Effect of Catalytic Upgrading of Pyrolysis Vapors in a Two-Stage Fixed-Bed Reactor. Energy & Fuels 2009. 23: p. 2248–2258.

[69] Pinheiro, A., et al., Impact of Oxygenated Compounds from Lignocellulosic Biomass Pyrolysis Oils on Gas Oil Hydrotreatment. Energy & Fuels 2009. 23: p. 1007–1014.

[70] Furimsky, E., Catalytic hydrodeoxygenation. Applied Catalysis A: General 2000. 199: p. 147–190.

[71] Yang, Y.Q., C.T. Tye, and K.J. Smith, Influence of MoS2 catalyst morphology on the hydrodeoxygenation of phenols. Catalysis Communications 2008. 9: p. 1364–1368.

[72] Kim, S.C. and F.E. Massoth, Kinetics of the Hydrodenitrogenation of Indole. Industrial & Engineering Chemistry Research, 2000. 39(6): p. 1705-1712.

[73] Laurent, E. and B. Delmon, Study of the hydrodeoxygenation of carbonyl, carboxylic and guaiacyl groups over sulfided CoMo/[gamma]-Al2O3 and NiMo/[gamma]-Al2O3 catalyst: II. Influence of water, ammonia and hydrogen sulfide. Applied Catalysis A: General, 1994. 109(1): p. 97-115.

[74] Yakovlev, V.A., et al., Development of new catalytic systems for upgraded bio-fuels production from bio-crude-oil and biodiesel. Catalysis Today, 2009. 144(3-4): p. 362.

[75] Odebunmi, E.O. and D.F. Ollis, Catalytic Hydrodeoxygenation I. Conversions of o-, p-, and m-Cresols. Journal of Catalysis 1983. 80: p. 56-64.

[76] Bejblova, M., et al., Hydrodeoxygenation of benzophenone on Pd catalysts. Applied Catalysis A: General 2005. 296: p. 169–175.

[77] Senol, O.I., et al., Effect of hydrogen sulphide on the hydrodeoxygenation of aromatic and aliphatic oxygenates on sulphided catalysts. Journal of Molecular Catalysis A: Chemical 2007. 277: p. 107-112.

[78] Laurent, E. and B. Delmon, Study of the hydrodeoxygenation of carbonyl, carboxylic and guaiacyl groups over sulfided CoMo/[gamma]-Al2O3 and NiMo/[gamma]-Al2O3 catalysts: I. Catalytic reaction schemes. Applied Catalysis A: General, 1994. 109(1): p. 77.

[79] Keane, M.A. and R. Larsson, Application of the Selective Energy Transfer Model to Account for an Isokinetic Response in the Gas Phase Reductive Cleavage of Hydroxyl, Carbonyl and Carboxyl Groups from Benzene Over Nickel/Silica. Catalysis Letters, 2009. 129(1-2): p. 93 -103.

[80] Viljava, T.R., R.S. Komulainen, and A.O.I. Krause, Effect of H2S on the stability of CoMo/Al2O3 catalysts during hydrodeoxygenation. Catalysis Today 2000. 60: p. 83-92.

[81] Lauritsen, J.V., et al., Atomic-scale insight into structure and morphology changes of MoS2 nanoclusters in hydrotreating catalysts. Journal of Catalysis, 2004. 221: p. 510–522.

[82] Puente, G.d.l., et al., Effects of Support Surface Chemistry in Hydrodeoxygenation Reactions over CoMo/Activated Carbon Sulfided Catalysts†. Langmuir 1999. 15: p. 5800-5806.

[83] Shin, E.-J. and M.A. Keane, Gas-Phase Hydrogenation/Hydrogenolysis of Phenol over Supported Nickel Catalysts. Industrial & Engineering Chemistry Research, 2000. 39(4): p. 883-892.

[84] Fiska, C.A., et al., Bio-oil upgrading over platinum catalysts using in situ generated hydrogen. Applied Catalysis A: General, 2009.

[85] Mori, A., et al., Palladium on carbon-diethylamine-mediated hydrodeoxygenation of phenol derivatives under mild conditions. Tetrahedron Letters, 2007. 63: p. 1270–1280.

[86] Procha´zkova, D., et al., Hydrodeoxygenation of aldehydes catalyzed by supported palladium catalysts. Applied Catalysis A: General 2007. 332: p. 56-64.

[87] Sebos, I., et al., Catalytic hydroprocessing of cottonseed oil in petroleum diesel mixtures for production of renewable diesel. Fuel 2009. 88: p. 145–149.

[88] Bui, V.N., et al., Co-processing of pyrolisis bio oils and gas oil for new generation of bio-fuels: Hydrodeoxygenation of guaïacol and SRGO mixed feed. Catalysis Today, 2009. 143(1-2): p. 172.

[89] Donnis, B., et al., Hydroprocessing of Bio-Oils and Oxygenates to Hydrocarbons. Understanding the Reaction Routes. Topics in Catalysis, 2009. 52(3): p. 229-240.

[90] Romero, Y., et al., Hydrodeoxygenation of benzofuran and its oxygenated derivatives (2,3-dihydrobenzofuran and 2-ethylphenol) over NiMoP/Al2O3 catalyst. Applied Catalysis A: General 2009. 353: p. 46-53.

[91] Bunch, A.Y. and U.S. Ozkan, Investigation of the Reaction Network of Benzofuran Hydrodeoxygenation over Sulfided and Reduced Ni–Mo/Al2O3 Catalysts. Journal of Catalysis 2002. 206: p. 177-187.

[92] Bunch, A.Y., X. Wang, and U.S. Ozkan, Hydrodeoxygenation of benzofuran over sulfided and reduced Ni–Mo/-Al2O3 catalysts: Effect of H2S. Journal of Molecular Catalysis A: Chemical 2007. 270: p. 264–272.

[93] Senol, O.İ., Hydrodeoxygenation of aliphatic andaromatic oxygenates on sulphided catalystsfor production of second generation biofuels, in Laboratory of Industrial Chemistry2007, Helsinki University of Technology: Finland.