# Production of hydrogen, alkanes and polyols by aqueous phase processing of wood-derived pyrolysis oils

**Tushar P. Vispute and George W. Huber***

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Pyrolysis oils are the cheapest liquid fuel derived from lignocellulosic biomass. However, pyrolysis oils are a very poor quality liquid fuel that cannot be used in conventional diesel and internal combustion engines. In this paper we show that hydrogen, alkanes (ranging from $C_1$ to $C_6$) and polyols (ethylene glycol, 1,2-propanediol, 1,4-butanediol) can be produced from the aqueous fraction of wood-derived pyrolysis oils (bio-oils). The pyrolysis oil was first phase separated into aqueous and non-aqueous fraction by addition of water. The aqueous phase of bio-oil contained sugars; anhydrosugars; acetic acid; hydroxyacetone; furfural and small amounts of guaiacols. The aqueous fraction was subjected to a low temperature hydrogenation with Ru/C catalyst at 125–175 °C and 68.9 bar. The hydrogenation step converts the various functionalities in the bio-oil (including aldehydes; acids; sugars) to corresponding alcohols. Undesired methane and light gases are also produced in this low-temperature hydrogenation step. Diols (ranging from C2 to C4) and sorbitol are obtained as major products in this step. After the low temperature hydrogenation step either hydrogen or alkanes can be produced by aqueous-phase reforming (APR) or aqueous-phase dehydration/hydrogenation (APD/H) respectively. APR was done with a 1 wt% $Pt/Al_2O_3$ catalyst at 265 °C and 55.1 bar. Hydrogen selectivities of up to 60% were observed. The hydrogen selectivity was a function of space velocity. A 4 wt% $Pt/SiO_2$-$Al_2O_3$ catalyst at 260 °C and 51.7 bar was used for alkane production by APD/H. The carbon conversion to gas phase products of 35% with alkane selectivity of 45% was obtained for a WHSV of 0.96 $h^{-1}$ when hydrogen is produced *in situ* from bio-oil. Alkane selectivity can be improved by supplying hydrogen externally. Alkane selectivities as high as 97% can be obtained when HCl is added to the aqueous-phase of the bio-oil and hydrogen is supplied externally. Model compounds for further bio-oil conversion studies are suggested.



## 1.0 Introduction

Diminishing petroleum resources combined with environmental concerns related to fossil fuels are making it increasingly important to find renewable and sustainable liquid fuel sources. The only sustainable source of carbon that can be used to make liquid fuels is carbon fixed by photosynthesis in plant biomass. Furthermore, bio-fuels, fuels derived from biomass, are the only sustainable liquid fuels.[1] Lignocellulosic biomass (which includes trees, grasses, energy crops and agricultural wastes) is currently the cheapest and most abundant form of plant biomass. However, there are many challenges associated with developing cost-effective processes for biomass conversion to liquid fuels. One very promising conversion technology is fast pyrolysis of biomass. Biomass fast pyrolysis involves rapidly heating the biomass without any external oxygen to intermediate temperatures producing a liquid product called bio-oil (or pyrolysis oil).

*Department of Chemical Engineering, University of Massachusetts, Amherst, 686 North Pleasant Street, Amherst, MA 01003, USA. E-mail: huber@ecs.umass.edu; Fax: +1 413-545-1647; Tel: +1 413-545-0276*

The bio-oil can be produced in weight yields as high as 75 wt% of the original dry biomass weight.[2] The bio-oil product typically contains 60–75% of the initial energy of the biomass.[3,4] Furthermore, fast pyrolysis has significantly lower capital and operating costs than competing technologies such as gasification and fermentation/hydrolysis.[5] A wide variety of feedstock can be used to produce bio-oil including wood, corn stover, agricultural waste and forest waste.

Bio-oil is the cheapest liquid fuel that can be made from lignocellulosic biomass.[5] However, the bio-oil is a very poor quality fuel that cannot be used in gasoline and diesel fuel engines for several reasons. Bio-oils have half the energy density compared to petroleum derived fuels due to their large oxygen content. Bio-oil is nearly insoluble with petroleum fuels. Bio-oils are acidic, having a pH of around 2.5. Bio-oils also degrade with time. Bio-oils are a complex mixture of more than 300 different compounds.[3,6] This mixture arises from the depolymerization and fragmentation of cellulose, hemicellulose and lignin, the three building blocks of the lignocellulosic biomass. Bio-oil, depending on its source, is found to contain various acids (formic, acetic, propanoic), aldehydes (acetaldehyde, hydroxyacetaldehyde), ketones (hydroxyacetone, hydroxybutanone, acetone), sugars (glucose, xylose, fructose), guaiacols, syringols, furans, furfurals and water.[3,7]

In spite of the difficulties of bio-oils they are very promising feedstocks for the production of conventional transportation fuels. The majority of effort of bio-oil conversion to date has focused on hydrotreating of the bio-oil and catalytic cracking of the bio-oil.[6,8–11] In this paper, we report a new approach for conversion of the bio-oil by aqueous phase processing (APP). Aqueous phase processing, developed by Dumesic and co-workers, involves the selective conversion of sugars and polyols to targeted hydrogen and alkanes.[12,13] The major advantage of this approach is that targeted products can be selectively produced by carefully controlling the chemistry that occurs in the aqueous phase. Other advantages of aqueous phase processing include: (1) liquid fuels can be made that can be used with gasoline and diesel engines, (2) high thermal efficiencies because the process occurs in the liquid phase, (3) no energetically-intense distillation steps, and (4) high rates of production per reactor volume. Liquid-phase catalytic processing of biomass-derived compounds offers unique opportunities for achieving high yields of specific, and well-defined, liquid fuels from biomass.

Hydrogen is an important reactant in a majority of refinery processes to make liquid fuels and biofuels.[14] Hydrogen can be produced in our process by aqueous-phase reforming (APR) which is a part of APP. APR involves C–C bond cleavage (to produce CO) followed by the water gas shift reaction over supported metal catalysts.[13] The overall reaction for APR of sorbitol is shown in eqn (1). Side reactions such as methanation and dehydration/hydrogenation take place to produce C1 to C6 alkanes as by-products.

$$C_6H_{14}O_6 + 6H_2O \rightarrow 6CO_2 + 13H_2 \quad (1)$$

Alkanes ranging from C1 to C6 can be produced more selectively by aqueous phase dehydration/hydrogenation (APD/H), also a subset of APP. This involves passing the aqueous solution of oxygenated hydrocarbon over a bi-functional catalyst containing metal and acidic sites such as Pt supported on silica-alumina. Hydrogen can be produced either *in situ* or *ex situ* on metal sites according to eqn (1). The alkanes are produced by dehydration reactions on solid acid sites to produce dehydrated products, and hydrogenation reactions on metal sites, as shown in eqn (2). If the alkane and hydrogen production reactions are balanced, then alkanes can be directly produced from sorbitol with $CO_2$ and $H_2O$ as the byproducts, as shown in eqn (3). Smaller alkanes are obtained as by-products due to the C–C bond cleaving reactions.

$$C_6H_{14}O_6 + 6H_2 \rightarrow C_6H_{14} + 6H_2O \quad (2)$$

$$(19/13)C_6H_{14}O_6 \rightarrow (36/13)CO_2 + C_6H_{12} + (42/13)H_2O \quad (3)$$

The majority of the previous APP work was done with pure compounds.[12,13,15] In this paper we show that APP chemistry can be extended for conversion of the aqueous fraction of bio-oil that is derived from lignocellulosic biomass. This involves the conversion of a large amount of functionalities to alkanes and hydrogen. This paper thus proposes a new route for production of renewable liquid fuels from biomass by combining fast pyrolysis with aqueous phase processing.

## 2.0 Experimental and materials

The bio-oil used in these studies was obtained from Renewable Oil International (ROI) LLC and was made from oak wood using ROI's fast pyrolysis process.[16,17] ROI uses a proprietary Auger reactor to make the bio-oils in high yield. The bio-oil was stored in the refrigerator to minimize ageing.

### 2.1 Elemental analysis, viscometry and catalyst characterization

Elemental analysis (C, H and O) of the bio-oil and its various fractions was done at Schwarzkopf Microanalytical Laboratory, Woodside, NY, USA. Ash content of the bio-oil was found by heating about 1 g of bio-oil in a furnace in presence of air at 600 °C for 6 hours. The amount of ash remaining was measured at the end of the run. The viscosity of the bio-oil and its various fractions was measured in a capillary glass viscometer (from Cannon Instrument Company). Viscosity measurement of the water insoluble bio-oil (WIBO) was carried out in a TA instrument, AR2000 using a concentric cylinders geometry. All the viscosity measurements were done at 25 °C. Catalysts were characterized by hydrogen chemisorption in a Quantachrome Autosorb 1C. About 0.1 g catalyst was loaded in a chemisorption cell and reduced. Reduction temperature regime was: room temperature to 260 °C at 30 °C $h^{-1}$ and hold at 260 °C for 2 h. The isotherms were then taken at 30 °C and 267, 533, 800, 1067 and 1333 N $m^{-2}$. The chemisorption cell was then evacuated for 30 minutes. Isotherms were again taken at 30 °C and 267, 533, 800, 1067 and 1333 N $m^{-2}$ to calculate the extent of physisorption. The amount of chemisorbed hydrogen was calculated from the difference between the two isotherms. The liquid samples were analyzed for the carbon content by a Shimadzu 5000A Total Organic Carbon (TOC) analyzer. The aqueous samples were further diluted by distilled water to a concentration below 1000 ppm carbon for the TOC analysis. The TOC samples were fortified with 0.5 N HCl (1.2 gm for 38.8 gm diluted sample) to remove dissolved $CO_2$. The TOC analyzer was standardized by sorbitol solutions of known concentrations.

### 2.2 Bio-oil extraction and pre-treatment

The bio-oil was mixed with distilled water to separate into two phases: an aqueous phase (WSBO: water soluble fraction of bio-oil) and an organic phase (WIBO: water insoluble bio-oil fraction). The mixture was then centrifuged in a Marathon 2100 centrifuge (Fisher Scientific) at 10 000 rpm for 30 minutes to ensure the phase separation. The two phases, aqueous (top) and non-aqueous (bottom), were then separated by decanting. The weight of the aqueous faction was measured to determine the amount of bio-oil that dissolved in water. For experimental purposes, 28 g of bio-oil was added to 112 g of water and mixed well. The aqueous and non-aqueous phases were separated by centrifugation followed by decanting. The resulting aqueous solution is about 13.4 wt% water soluble bio-oil in water, which is about 5 wt% carbon in water. This aqueous solution was used in the batch hydrogenation experiments. The product of batch hydrogenation was further diluted to about 2 wt% carbon in water. This solution was then used as the feed for further APP

experiments. In the remaining part of the paper this will be called WSBO.

### 2.3 Hydrogenation of aqueous fraction of bio-oil

Hydrogenation of the aqueous fraction of the bio-oil was carried out in a 170 ml Parr batch reactor. About 80 ml of the aqueous fraction of the bio-oil (about 5 wt% carbon) was loaded in the reactor along with 3–4 g (wet basis, 50 wt% moisture content) of 5 wt% Ru/activated C catalyst (Strem Chemicals, Product No. 44–4059). The reactor was then purged at least 4–5 times with helium gas to get rid of the air present in the reaction vessel. The reactor was then purged with hydrogen at least 4–5 times to replace all the helium with hydrogen. The reactor pressure was set to 48.3 bar by adding hydrogen and the heating and stirring were started. Once the temperature reached the desired value, the reactor pressure was increased to 68.9 bar total by adding more hydrogen. Additional hydrogen was added to the reactor during the course of reaction to compensate for the hydrogen consumption. The total pressure was maintained at 68.9 bar. The amount of hydrogen consumed during the reaction was calculated from the decrease in pressure. Liquid samples were withdrawn during the run from the liquid sampling tube. The liquid samples were filtered before analysis to remove the catalyst particles. The liquid samples as well as the reactant and the final product of the batch hydrogenation were analyzed for carbon content by a TOC analyzer. The product and feed compositions were measured with a Shimadzu gas chromatograph (GC) (model 2010) and a high performance liquid chromatograph (HPLC). A flame ionization detector (FID) was used on the GC to quantify all the reactants and products except sugars, sugar alcohol and levoglucosan. The reactants and products were also verified by GC-MS. A Restek Rtx-VMS (Catalog No. 19915) column was used with a constant column linear velocity of 31.3 cm $s^{-1}$. Ultra high purity helium was used as the carrier gas; injector and detector were both held at 240 °C. The GC oven was programmed with following temperature regime: hold at 35 °C for 5 min, ramp to 240 °C at 10 °C $min^{-1}$ and hold at 240 °C for 5 min. On HPLC, an RI detector (held at 30 °C) was used to quantify sugars, sugar alcohol and levoglucosan in the feed and product of batch hydrogenation. Bio-Rad's Aminex HPX-87H column (Catalog No. 125–0140) was used with distilled water as the mobile phase with the flow rate of 1 ml $min^{-1}$. The column oven temperature was held constant at 30 °C.

### 2.4 Aqueous phase processing

The hydrogenated aqueous fraction of the bio-oil was diluted by the addition of distilled water to about 2 wt% carbon in water. This diluted product was used as the feed for the further liquid phase processing. The hydrogenation of the aqueous fraction of bio-oil was carried out at 175 °C and 68.9 bar total pressure for 3 hours. A $\frac{1}{4}''$ or $\frac{1}{2}''$ stainless steel tube was packed with the reforming or dehydration/hydrogenation catalyst with glass wool plugs on both the sides. The catalyst used for reforming was 1 wt% $Pt/Al_2O_3$, and was obtained from the UOP research center (Product No. 4761–137). The dehydration/hydrogenation catalyst was 4 wt% $Pt/SiO_2$-$Al_2O_3$ and was prepared by the incipient wetness method. The appropriate amount of the solution of tetraammineplatinum (II) nitrate (Strem Chemicals, Product No. 78–2010) in distilled water was added drop wise to the silica-alumina powder ($SiO_2$ to $Al_2O_3$ ratio = 4, Davison SIAL 3125) with continuous mixing. The wet catalyst was then dried in an oven at 80 °C for 7–8 h. The catalyst was then calcined in air flowing at 300 ml $min^{-1}$. The temperature regime for calcining was: room temperature to 260 °C in 3 h, then hold at 260 °C for 2 h. Both the catalysts ($Pt/Al_2O_3$ and $Pt/SiO_2$-$Al_2O_3$) were reduced in the flow reactor with hydrogen flowing from the bottom at about 200 ml $min^{-1}$. The temperature regime used for reduction of $Pt/SiO_2$-$Al_2O_3$ catalyst was: room temperature to 450 °C at 50 °C $h^{-1}$, then hold at 450 °C for 2 h. The temperature regime used for reducing $Pt/Al_2O_3$ catalyst was: room temperature to 260 °C at 30 °C $h^{-1}$, then hold at 260 °C for 2 h.

The reactor tube was heated by a Lindberg (type 54032) furnace. The liquid feed was fed to the reactor from the bottom with the help of a JASCO PU980 HPLC pump at the rate of 0.04 ml $min^{-1}$. A gas–liquid separator was employed after the reactor tube. Helium was supplied from the top as the carrier gas at flow rates from 30 ml $min^{-1}$ to 60 ml $min^{-1}$. The gaseous products from the reactor (and helium carrier gas) flow through a back pressure regulator, used to maintain the pressure of the reaction system. External hydrogen, required for catalyst reduction (~200 ml $min^{-1}$) or for the reaction (was ~100 ml $min^{-1}$) supplied from the bottom of the reactor. No carrier gas was used when hydrogen was supplied externally. The gaseous products were further analyzed by two online gas chromatographs (HP 5890 series II). Permanent gases in the gaseous product ($CO_2$ and $H_2$) were analyzed by a thermal conductivity detector (TCD). An Alltech HAYESEP DB 100/120 packed column (Part No. 2836PC) was used with the oven temperature held constant at 75 °C. The TCD and the injection port were held at 160 °C and 120 °C, respectively. The column flow rate was 1 ml $min^{-1}$ with helium as carrier gas. Alkanes in the gaseous product were analyzed on a FID with an Alltech AT-Q capillary column (Part No. 13950). Helium was used as the carrier gas with a column flow rate of 1 ml $min^{-1}$. The injection port and the detector were both held at 200 °C. The following GC oven temperature regime was used: hold at 40 °C for 6 min, ramp to 180 °C at 5 °C $min^{-1}$ and hold at 180 °C for 25 min. Carbon selectivity to a particular alkane was calculated by dividing the carbon moles in a particular alkane by total carbon moles in all of the alkanes. For a particular catalyst loaded in the reactor, liquid feed was started at time $t = 0$. Steady state was usually reached within 8 hours. At least 3 gas samples were analyzed to ensure the steady state. Liquid product accumulated in the gas–liquid separator was drained then. The liquid product was analyzed for the carbon content. Reaction parameters were then changed for further studies. Time on stream for a particular catalyst from the start of reaction ($t = 0$) was noted for each sample and was denoted by time on stream for that catalyst.

## 3.0 Results

### 3.1 Characterization of bio-oil

Various characterization techniques were used to characterize the bio-oil. Physical characterization was done by viscosity and solubility measurements. GC-MS was used to identify the

components. GC-MS, GC-FID and HPLC were used for the quantification of the components.

**3.1.1 Elemental analysis.** Elemental analysis of the oak wood bio-oil was found to be 47.0 wt% carbon, 8.2 wt% hydrogen and the rest oxygen. Nitrogen was not detected. The oxygen content of 44.8 wt% is higher as compared to the typical bio-oil compositions. Typical bio-oil oxygen content is in the range of 35 to 40 wt%.[18] In addition to carbon, oxygen and hydrogen, nitrogen (0 to 0.2 wt%) can be present in the bio-oil.[6] Mineral components of the bio-mass (including potassium, sodium, calcium and magnesium) also end up in the bio-oil in trace quantities.[3] Typical ash content of bio-oils is 0–0.2 wt%.[6] The ash content of our bio-oil was 0.3 wt%.

**3.1.2 Solubility studies.** Upgrading of the bio-oil without using any solvent is preferred if possible. However, this route has many problems, such as high viscosity and thermal instability of bio-oil, clogging of reactors, considerable coking, and catalyst deactivation due to coking. Bio-oil can be dissolved in a suitable solvent and then treated for upgrading to help with these problems. The oak wood bio-oil used in this study was found to be almost completely miscible in methanol, iso-propanol and acetone with some residue left that can be filtered. About 14 wt% of the bio-oil was found to be soluble in toluene, which is a gasoline like solvent. Solubility of the bio-oil in diesel fuel was about 4 wt%. The solubilities were measured by mixing bio-oil and solvent in 1:1 proportion at room temperature and the two layers formed were separated by decanting after centrifugation. Toluene and diesel fuel fractions were found to consist of various guaiacols. Low solubility of bio-oil in toluene and diesel fuel signifies its incompatibility with the conventional liquid transportation fuels. An ideal solvent for hydroprocessing of the bio-oil should dissolve a considerable fraction of bio-oil in it and should be inert to hydrogenation. Alcohols such as methanol and iso-propanol are not inert to the hydrogenation. Whereas gasoline, diesel fuel or any saturated liquid alkane are inert to hydrogenation but are incompatible with the bio-oil.

Two phases form when our bio-oil is mixed with water at a water to bio-oil weight ratio of greater than 1 to 4. For the bio-oil in this study, about 60 to 65 wt% of the bio-oil is soluble in water irrespective of the amount of water added. Water is inert for hydrogenation. Furthermore, a significant fraction of the bio-oil is water soluble, making water an ideal solvent for hydroprocessing of bio-oil. The elemental analysis for mixing bio-oil with water is shown in Fig. 1 for a water to bio-oil weight mixture of 1 : 1. As can be seen in this figure the WSBO has a higher oxygen content than the WIBO. About 62 wt% of the original bio-oil is in the aqueous phase. This also includes water that was present in the bio-oil. Our findings are similar to those of Sipila *et al.*, where 60 wt% of the bio-oil (made from mixed maple and oak wood) was found to be water soluble.[19]

The water insoluble bio-oil (WIBO) was mixed with methanol and analyzed by GC-MS. It mainly consists of guaiacol and its substituted forms which are known to come from the lignin part of the wood. The WSBO was analyzed with GC-MS, GC-FID, HPLC and TOC as shown in Table 1. The major components of the aqueous fraction are acetic acid, hydroxyacetone, hydroxyacetaldehyde, levoglucosan, furfural, 2-furanone and sugars. We were only able to identify 60% of the carbon in the aqueous fraction of the bio-oil with our methods used in this study. This did, however, help us in understanding some of the bio-oil conversion reactions. The rest of the carbon was probably present in the form of compounds like formic acid, various furans, and higher molecular weight sugars (*i.e.* cellobioses and trioses). The column used in HPLC can separate sugar, sugar alcohols and anhydro sugars. But it cannot separate various sugars from each other. A broad peak was observed for sugars in HPLC. Various sugars may be present, including glucsoe, xylose, fructose, mannose and galactose. Piskorz *et al.* have identified hydroxyacetaldehyde up to 10 wt% in the bio-oil.[20] We found that only 1.5% of the carbon in WSBO was from hydroxyacetaldehyde. Formic acid could not be observed in our solution due to the large amounts of water we used and hence is not quantified here. High molecular weight degradation products of pentoses, hexoses are also present in the bio-oil[3] and were not detected by our analytical methods. Cellobiosan is known to be present in bio-oil in a significant amount.[19,21] Luo *et al.* have identified phenolic compounds (phenol and its alkyl derivatives) up to 20 wt% in a bio-oil made from *P. indicus*.[22] Phenol and its alkyl derivatives were not detected in significant amounts in the bio-oil we used for this study.

**Table 1** Identification of major components of aqueous fraction of bio-oil. The aqueous fraction of bio-oil was made by mixing 80 g of water with 9 g of bio-oil

| Quantification method | Species | Concentration (mmole carbon $L^{-1}$) | % of total carbon |
|---|---|---|---|
| GC-FID | Hydroxyacetone | 135.5 | 6.5 |
| GC-FID | Hydroxyacetaldehyde | 28.1 | 1.4 |
| GC-FID | Guaiacols and derivatives | 30.8 | 1.5 |
| HPLC | Sugars | 377.4 | 18.2 |
| HPLC | Levoglucosan | 390.6 | 18.8 |
| GC-FID | Acetic acid | 182.2 | 8.8 |
| GC-MS | Furfural and 2-furanone | 100.0 | 4.8 |
| | Total carbon content identified by GC & HPLC | 1244.6 | 60.0 |
| | Total carbon content measured by TOC | 2075.9 | 100 |

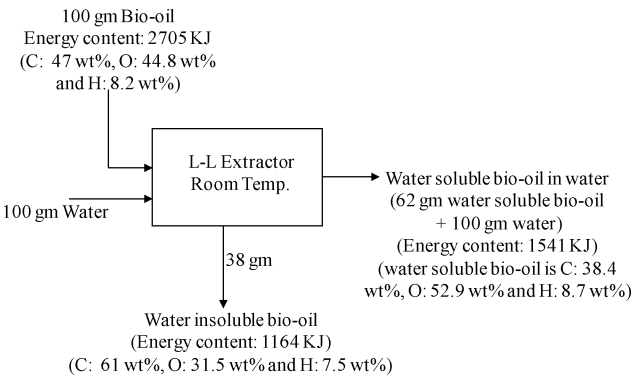



**Fig. 1** Liquid–liquid extraction of the bio-oil in water.

**3.1.3 Viscosity measurements.** The various bio-oil fractions have a wide range of viscosities, which are probably due to both intramolecular and intermolecular interactions. Bio-oils are also known to undergo viscosity changes during ageing



**Table 2** Viscosity of the bio-oil, bio-oil fractions and bio-oil mixtures

| | Viscosity[a]/cP |
|---|---|
| Bio-oil | 153 |
| 80 wt% bio-oil in methanol | 17.1 |
| 50 wt% bio-oil in methanol | 2.93 |
| 20 wt% bio-oil in methanol | 1.01 |
| Water insoluble bio-oil[b] | 50 000 |
| 80 wt% water insoluble bio-oil in methanol | 95.1 |
| 50 wt% water insoluble bio-oil in methanol | 5.1 |
| 20 wt% water insoluble bio-oil in methanol | 1.04 |
| Water soluble bio-oil solution[c] | 1.65 |

[a] All the viscosity measurements are done in a capillary glass viscometer (except for the water insoluble bio-oil) at 25 °C. [b] TA instrument AR2000 used with concentric cylinders geometry. [c] Solution was 50 wt% water soluble bio-oil in water.

and bio-oil upgrading.[10,23] Table 2 shows the viscosity of bio-oil, bio-oil mixtures and bio-oil fractions prior to upgrading. The oak wood bio-oil used in our studies was found to have the viscosity of 153 cP at 25 °C. Typical viscosity values of the bio-oil reported in the literature depicts an order of magnitude variation. According to Bridgwater *et al.*, the viscosity of bio-oils ranges from 30 to 200 cP at 40 °C.[24] The viscosity can be as high as 1000 cP at 40 °C depending on the feedstock and process conditions.[6] The viscosity of the bio-oil decreases exponentially upon addition of small amount of solvents. As shown in Table 2, addition of 20 wt% of methanol to bio-oil results in an order of magnitude decrease in the viscosity.

The water insoluble bio-oil is a highly viscous sticky brown liquid with a viscosity of more than 50 000 cP. Its viscosity also decreases exponentially upon addition of methanol. The phenolic compounds originating from lignin are present in the bio-oil as both monomeric and oligomeric compounds.[3] These phenolic compounds are present in significantly higher concentrations in the WIBO than in the water soluble bio-oil. These high molecular weight oligomers (molecular weight up to 5000) can form networks due to intermolecular interactions, resulting in high viscosity of the bio-oil. A rheological study of bio-oil obtained from the soft wood bark residue indicates the existence of self-aggregating intermolecular interactions forming long-range network structures.[25] These interactions will be stronger in the water insoluble bio-oil due to its concentrated nature, explaining the very high viscosity observed for it. Addition of methanol to bio-oil or WIBO results in disrupting of the intermolecular network due to solvation, significantly reducing the viscosity.

### 3.2 Low temperature hydrogenation of the aqueous fraction of bio-oil

The aqueous fraction of bio-oil contains thermally unstable compounds (*e.g.* glucose, levoglucosan) that decompose when heated to high temperature. These compounds must be converted into thermally stable compounds prior to APP.[12,13] If they are not converted to thermally stable compounds then they can cause deactivation of the catalyst by coke formation. The thermally unstable compounds can be converted to thermally stable compounds by a low temperature aqueous phase hydrogenation. In the low temperature hydrogenation, compounds such as hydroxyacetaldehyde, hydroxyacetone, and furfural are converted to corresponding alcohols such as ethylene glycol, propylene glycol and tetrahydrofurfuryl alcohol, respectively. The challenge with the low temperature aqueous phase hydrogenation step is to selectively hydrogenate targeted C–O bonds and not break C–C or C–O bonds. Cleavage of C–C and C–O bonds results in formation of lighter products including undesired methane. The aqueous phase hydrogenation reactions in this study were all performed in a batch reactor.

Batch hydrogenation of the aqueous fraction of bio-oil was done in the temperature range of 125–175 °C with a 5 wt% Ru/Carbon catalyst. The hydrogen uptake of this catalyst was 33.2 μmol H $g^{-1}$ dry catalyst, which corresponds to a surface to bulk Ru ratio of 6.7%. Table 3 depicts the data gathered for batch hydrogenation where the temperature is increased in steps from 125 °C to 150 °C to 175 °C. Ethylene glycol, propylene glycol, butanediols, tetrahydrofurfuryl alcohol, γ-butyrolactone and 1,2-cyclohexanediol all reach their respective maximum concentrations within 2.5 h at 125 °C. All the hydroxyacetone is also consumed during this same period. Acetic acid does not react at the reaction conditions used.

Sugars and levoglucosan do not undergo complete conversion at 125 °C. Levoglucosan has a very slow rate of hydrogenation at 125 °C. Initially, levoglucosan concentration decreases rapidly from 390.6 mmol-C $L^{-1}$ to about 275 mmol-C $L^{-1}$ at 125 °C. However, it then stays the same for 3 h. The levoglucosan concentration does decrease when the temperature is increased further. This implies that the high reaction temperature is required for the hydrogenation of levoglucosan. Levoglucosan is converted to sorbitol in two steps, hydrolysis of levoglucosan to glucose,[21] followed by hydrogenation of glucose to sorbitol. The first reaction is an acid catalyzed reaction, whereas the second reaction is catalyzed by a hydrogenation catalyst, in this case Ru/C. In the absence of any externally added acid in the reaction mixture, it is possible that the first reaction is catalyzed by acids that are present in the aqueous fraction of bio-oil. Disappearance of the sugars follow a similar but less obvious trend as levoglucosan. At 125 °C, sugars (377 mmol-C $L^{-1}$ to 175 mmol-C $L^{-1}$) disappear twice as fast as levoglucosan (390 mmol-C $L^{-1}$ to 275 mmol-C $L^{-1}$) does in 3.5 hours. This implies that the first step (levoglucosan to glucose) is the slower one and hence the rate limiting step in the conversion of levoglucosan to sorbitol. Increasing the acidity of the feed could therefore help expedite the conversion of levoglucosan to sorbitol.[21]

A low hydrogenation temperature is preferred to minimize carbon loss from liquid in the form of methane. About 25% of carbon is converted to methane at 175 °C, whereas at 125 °C, only about 10% carbon is converted to methane. However, sugars and levoglucosan are not completely converted to corresponding alcohols at 125 °C for shorter reaction times (<3.5 h). Thus, there requires some optimization of reaction temperature and time. At high temperature, shorter reaction times (just sufficient to convert all the reactants to desired products) should be used to keep carbon loss to methane low. At low temperature, longer reaction time may be required to convert the reactants to respective alcohols. Hydrogen is consumed during the hydrogenation step (see Table 3).

Hydrogen consumption is about 0.034 g/g water soluble bio-oil at 125 °C and doubles for every 25 °C rise in the temperature.

**Table 3** Hydrogenation of the aqueous fraction of bio-oil with initial carbon concentration of 24 900 mg $L^{-1}$ (by TOC), catalyst: 3 gm of 5 wt% Ru/C (wet basis), total *P*: 68.9 bar

| | Temperature/°C | 25 | 125 | 125 | 125 | 125 | 150 | 150 | 150 | 175 | 175 | 175 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Minutes* | *0* | *30* | *60* | *150* | *210* | *270* | *320* | *360* | *400* | *455* | *545* |
| Method | | Concentration/mmol-C $L^{-1}$ | | | | | | | | | | |
| GC-FID | Hydroxyacetone | 135.5 | 55.7 | 24.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| GC-FID | Hydroxyacetaldehyde | 28.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| GC-FID | Ethylene glycol | 0.0 | 90.6 | 172.3 | 212.2 | 216.9 | 198.9 | 191.6 | 204.6 | 222.6 | 210.9 | 197.3 |
| GC-FID | Propylene glycol | 0.0 | 25.4 | 113.1 | 159.0 | 164.1 | 154.9 | 163.0 | 172.5 | 186.6 | 182.7 | 171.0 |
| GC-FID | Butanediols[a] | 0.0 | 13.3 | 36.6 | 52.7 | 55.5 | 51.8 | 59.1 | 63.0 | 64.3 | 61.1 | 57.9 |
| GC-FID | THFA[b] | 0.0 | 9.9 | 12.5 | 15.7 | 14.9 | 13.5 | 11.4 | 13.3 | 12.0 | 15.0 | 18.0 |
| GC-FID | γ-Butyrolactone | 0.0 | 24.7 | 31.7 | 30.4 | 29.4 | 30.5 | 30.3 | 30.7 | 30.8 | 29.8 | 26.9 |
| GC-FID | Guaiacols[c] | 30.8 | 28.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| HPLC | Sugars | 377.4 | 242.5 | 232.6 | N.A. | 174.7 | 140.4 | 125.9 | 117.7 | 80.4 | 67.3 | 47.5 |
| HPLC | Sorbitol | 0.0 | 0.0 | 0.0 | N.A. | 56.6 | 89.8 | 117.1 | 141.2 | 186.7 | 204.7 | 213.8 |
| HPLC | Levoglucosan | 390.6 | 274.8 | 271.4 | N.A. | 276.7 | 235.8 | 216.0 | 212.9 | 150.7 | 132.0 | 123.6 |
| GC-FID | Acetic acid | 182.2 | 126.1 | 192.6 | 170.9 | 167.1 | 186.0 | 196.3 | 201.1 | 206.8 | 210.2 | 202.6 |
| | Total mmol-C $L^{-1}$ | 1144.5 | 891.8 | 1087.2 | N. A. | 1155.9 | 1101.7 | 1110.8 | 1157 | 1141.0 | 1114 | 1058.6 |
| | % C identified in liquid | 55.2 | 50.5 | 59.8 | N. A. | 63.8 | 59.6 | 61.8 | 61.7 | 64.6 | 63.8 | 63.0 |
| | % C in liquid by TOC | 100.0 | 85.1 | 87.6 | 86.1 | 87.3 | 89.2 | 86.7 | N.A. | 85.1 | 84.2 | 81.0 |
| | $H_2$ Consumption (g/g WSBO) | 0 | 0.007 | 0.016 | 0.024 | 0.034 | 0.038 | 0.048 | 0.061 | 0.070 | 0.091 | 0.120 |

[a] 1,2 and 1,4-butanediol. [b] Tetrahydrofurfuryl alcohol. [c] Contains guaiacol and methyl guaiacol, N.A. = not analyzed.



Hydrogen consumption at the end of the run was found to be 0.12 g/g water soluble bio-oil. Hydrogen consumption should be minimized by using as low temperature as possible. At low temperature unwanted reactions, such as saturation of aromatic rings, which consume a considerable amount of hydrogen, are suppressed. The hydrogen consumption at low temperature (125 °C) is comparable to that reported by Baker and Elliott for the two stage hydroprocessing process, where 0.034 gm $H_2$ is consumed per gm of bio-oil.[8]

### 3.3 Aqueous-phase reforming of the aqueous fraction of Bio-oil

We produced hydrogen from the aqueous fraction of the bio-oil by passing it over a 1 wt% $Pt/Al_2O_3$ catalyst as shown in Table 4 and Fig. 2. The $Pt/Al_2O_3$ catalyst had a hydrogen uptake of 40.6 μmol H $g^{-1}$ catalyst which corresponds to a surface to bulk metal ratio of 79.2%. The concentration of the WSBO in water was 4–5 wt% or 1.5–2 wt% carbon in water.

The concentration varied depending on the pretreatment of the bio-oil. Prior to each run the exact carbon content of the

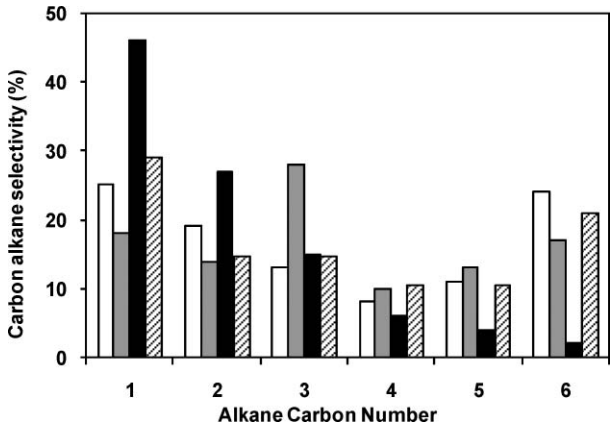



**Fig. 2** Alkane distribution for aqueous-phase reforming of WSBO and 5 wt% sorbitol solution at 265 °C and 55.1 bar with 1 wt% $Pt/Al_2O_3$ catalyst. Feed and reaction key (see Table 4) (□) WSBO-A, (■) WSBO-B, (▨), (■) Sorbitol, (▨) WSBO-C.

**Table 4** Aqueous-phase reforming of WSBO and 5 wt% sorbitol solution with a 1 wt% $Pt/Al_2O_3$ catalyst. Reaction conditions: 265 °C and 55.1 psi. The WSBO contains 1.5–2 wt% carbon and is prepared by hydrogenation of the aqueous fraction of bio-oil at 175 °C and 68.9 bar with a 5 wt% Ru/C catalyst for 3 h

| Run code | Feed pre-treatment | WHSV/$h^{-1}$[a] | Hours catalyst on stream | $H_2$ selectivity[b] (%) | Alkane selectivity[c] (%) | % Carbon in gas phase effluent[d] | % Carbon in liquid phase effluent |
|---|---|---|---|---|---|---|---|
| WSBO-A | Hydrogenation | 0.73 | 75 | 60 | 21 | 21 | 73 |
| WSBO-B | Hydrogenation | 0.13 | 20 | 50 | 35 | 41 | 43 |
| WSBO-C | None | 0.73 | 10 | 36 | 30 | 32[e] | 22 |
| Sorbitol | None | 0.73 | 34 | 64 | 16 | 44[f] | 51 |

[a] WHSV = flow rate of the aqueous fraction of bio-oil (g $h^{-1}$) divided by grams of catalyst in the reactor. [b] $H_2$ selectivity = (molecules $H_2$ produced/C atoms in gas phase) × (1/reforming ratio) × 100, reforming ratio (RR) is the ratio of molecules of $H_2$ produced to C atoms in the gas phase assuming that all the water soluble bio-oil goes to $H_2$ and $CO_2$ only, for hydrogenated water soluble bio-oil RR is 3, RR for sorbitol is 13/6. [c] Alkane selectivity = (total moles of carbon atoms in alkane products)/(total moles of carbon atoms in the feed) × 100. [d] Gas phase contains C1 to C6 alkanes, $CO_2$ and $H_2$. [e] Decreases to 23% with the catalyst on stream for 22 h. [f] Decreases to 38% with the catalyst on stream for 48 h.

**Table 5** Production of alkanes from WSBO and sorbitol with a 4 wt% $Pt/SiO_2$–$Al_2O_3$ catalyst. Reaction conditions: 260 °C and 51.7 bar. The WSBO feeds contain 1.5–2 wt% carbon and are prepared by hydrogenation of the aqueous fraction of bio-oil at 175 °C and 68.9 bar with a 5 wt% Ru/C catalyst for 3 h.

| Run code | Feed | WHSV[a] ($h^{-1}$) | Hours catalyst on stream | Alkane selectivity[b] (%) | % Carbon in gas phase effluent[c] | % Carbon in liquid phase effluent |
|---|---|---|---|---|---|---|
| WSBO-D | WSBO | 0.96 | 48 | 45 | 35[d] | 38 |
| WSBO-E | WSBO | 0.20 | 25 | 42 | 40–50 | 43 |
| WSBO-D-$H_2$ | WSBO + $H_2$ | 0.96 | 80 | 77 | 18 | 59 |
| WSBO-E-$H_2$ | WSBO + $H_2$ | 0.20 | 55 | 85 | 56 | 37 |
| WSBO-HCl | WSBO + HCl | 0.20 | 200 | 55–60 | 40–45 | 47 |
| WSBO-HCl-$H_2$ | WSBO + HCl + $H_2$ | 0.20 | 215 | 97 | 55–60 | 32 |
| Sorbitol | Sorbitol | 0.96 | 24 | 42 | 72 | 19 |

[a] WHSV = flow rate of the aqueous fraction of bio-oil (g $h^{-1}$) divided by grams of catalyst in the reactor. [b] Alkane selectivity = (total moles of carbon atoms in alkane products)/(total moles of carbon atoms in the feed) × 100. [c] Gas phase contains C1 to C6 alkanes and $CO_2$. [d] Decreases to 30% with the catalyst on stream for 60 h.



feed was measured with TOC. The liquid phase carbon content was measured by TOC analysis of the feed and liquid products. The gas phase contained C1 to C6 alkanes, $CO_2$ and $H_2$ for all products tested.

The carbon conversion to gas phase products was just above 20% for the hydrogenated aqueous fraction of bio-oil (WSBO-A) at WHSV of 0.73 $h^{-1}$. The $H_2$ and alkane selectivities were 60% and 21% respectively. This indicates that at low conversion, high hydrogen selectivity can be obtained from the aqueous fraction of bio-oil. At similar conditions, sorbitol had a carbon conversion of 44% and $H_2$ and alkane selectivity of 64% and 16% respectively. Decreasing the WHSV to 0.13 $h^{-1}$ for the WSBO (WSBO-B) increases the gas phase conversion to 41%. At this higher conversion, the hydrogen selectivity decreases to 50%. Thus, the hydrogen and alkane selectivities are a function of the gas phase conversion. When WSBO-B data is compared to sorbirtol (both have similar conversion), it can be concluded that the aqueous fraction of the bio-oil is less active than sorbitol. The alkane selectivity for the WSBO and sorbitol are significantly different, as shown in Fig. 2. The WSBO more selectively produces the heavier alkanes as compared to the sorbitol.

Our results are similar to that of Cortright *et al.* who produced hydrogen from 1 wt% sorbitol solution at 265 °C and 55.1 bar with a 3 wt% $Pt/Al_2O_3$ catalyst.[13] Carbon conversion to gas phase, $CO_2$ selectivity and hydrogen selectivity of 90%, 68% and 46% respectively, were reported. The difference between our runs and that of Cortright *et al.* is that our catalyst had significantly fewer surface sites (40.6 μmol H $g^{-1}$ catalyst of hydrogen uptake *vs.* 105 μmol $g^{-1}$ catalyst of CO uptake). Also the sorbitol space velocity used by Cortright *et al.* is 0.008 g sorbitol per gram catalyst as compared to our 0.0365 g sorbitol per gram catalyst. To compare our catalyst to that of Cortright *et al.*, we fed our reactor with 5 wt% sorbitol in water with same operating conditions. Conversion to gas phase, $CO_2$ selectivity and hydrogen selectivity for sorbitol were 44%, 84% and 64%, respectively. We see low activity for sorbitol due the low catalyst concentration and less active catalyst we used.

Reforming of a non-hydrogenated aqueous fraction of the bio-oil (WSBO-C) was also studied at WHSV of 0.73 $h^{-1}$. The gas phase conversion decreased from 32% at 10 h to 23% at 22 h. A hydrogen selectivity of only 36% was observed with non-hydrogenated water soluble bio-oil, demonstrating the necessity of the hydrogenation step.

### 3.4 Liquid phase dehydration/hydrogenation of aqueous fraction of bio-oil

Alkanes can be produced from the aqueous fraction of the bio-oil by aqueous-phase dehydration/hydrogenation with a bi-functional catalyst.[12] Platinum supported on silica-alumina is the catalyst used in these studies. The reactions that occur on Pt include hydrogenation; reforming and water–gas shift. The acidic silica-alumina catalyzes dehydration reactions. The data gathered with 4 wt% $Pt/Al_2O_3$-$SiO_2$ catalyst is depicted in Table 5 and in Fig. 3 and 4. This data was collected on the hydrogenated WSBO with hydrogen as a co-feed and without hydrogen as a co-feed. The concentration of WSBO in water was 4–5 wt%, which is 1.5–2 wt% carbon in water.

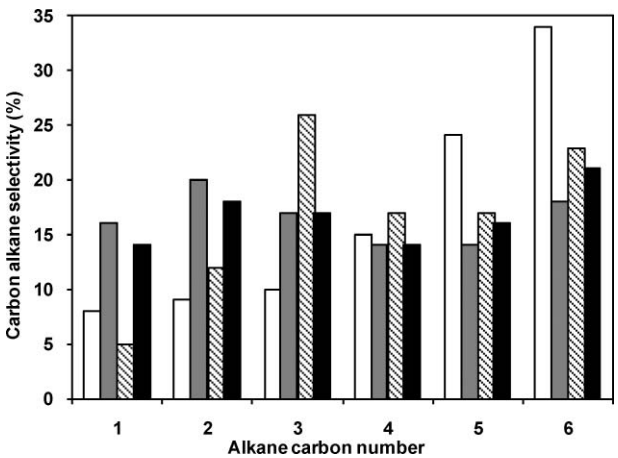



**Fig. 3** Alkane distribution for the liquid phase dehydration/hydrogenation of WSBO and 5 wt% sorbitol solution at 260 °C and 51.5 bar with 4 wt% $Pt/SiO_2$-$Al_2O_3$ catalyst. Feed and reaction key (see Table 5): (□) WSBO-D, (■) WSBO-E, (▨) WSBO-HCl, (■) sorbitol.

The WSBO was tested at two different space velocities (WSBO-D and WSBO-E) without adding hydrogen as a feed. The carbon conversion to gas phase products increased from 35% to 40–50% when the WHSV decreased from 0.96 $h^{-1}$ to

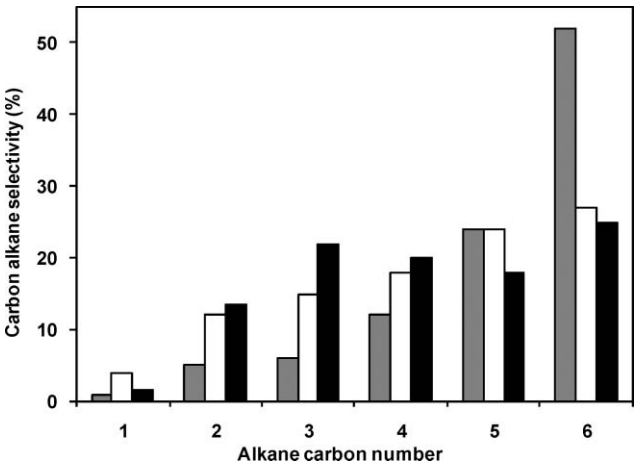



**Fig. 4** Alkane distribution for the liquid phase dehydration/hydrogenation of WSBO at 260 °C and 51.7 bar with 4 wt% $Pt/SiO_2$-$Al_2O_3$ catalyst. Feed and reaction key (see Table 5): (■) WSBO-D-$H_2$, (□) WSBO-E-$H_2$, (■) WSBO-HCl-$H_2$.

0.2 $h^{-1}$. The alkane carbon selectivity was 45% for WSBO-D with hexane and pentane being the most abundant alkanes (see Fig. 3). A similar (42%) alkane selectivity is observed at both the space velocities. However, the alkane distribution shifts towards lower alkanes at higher conversions (see Fig. 3). At similar operating conditions to the WSBO, sorbitol had a carbon conversion of 72% with the alkane selectivity of 42%. The sorbitol shows a similar distribution of C1-C6 alkanes as the WSBO. For sorbitol (72% conversion) and WSBO-E (up to 50% converison), similar alkane selectivity (42%) is observed. Bio-oil is clearly less active than pure sorbitol for alkane production, but comparable alkane selectivites can be achieved. Huber *et al.* reported 95% conversion with 60% alkane selectivity for sorbitol with the same temperature, pressure, catalyst concentration and a WHSV of 1.3 $h^{-1}$.[12] Our catalyst is less active for dehydration/hydrogenation as compared to that of Huber *et al.* As the time of on stream increases from 48 h to 60 h the conversion for WSBO-D decreases from 35% to 30%, indicating catalyst deactivation.

Hydrogen was supplied externally to improve the carbon selectivity towards alkanes (WSBO-D-$H_2$ and WSBO-E-$H_2$).[12] The alkane selectivity increases when hydrogen is added from 42–45% to 77–85%. This is due to the suppression of hydrogen producing reforming reactions in the presence of external hydrogen. Catalyst deactivation can be the reason for the low conversion observed as the WSBO-D-$H_2$ data was gathered on the same catalyst after the collection of WSBO-D data. At low WHSV (0.2 $h^{-1}$), carbon conversion was 56% with 85% alkane selectivity when the hydrogen was supplied externally (WSBO-E-$H_2$). When hydrogen is supplied externally, very high hexane and pentane selectivities are observed with almost complete suppression of methane formation (Fig. 4). However the hexane and pentane carbon selectivity does decrease with increasing conversion (Fig. 4).

The alkane selectivity is a function of relative rates of dehydration and hydrogenation reactions. Hydrochloric acid was added to the reaction mixture to increase the rate of dehydration reactions. HCl was added to the aqueous fraction of bio-oil before the hydrogenation step to a HCl concentration of 1 wt%. The product was then subjected to the aqueous phase dehydration/hydrogenation. The gas phase carbon conversion did not increase when HCl was added. However, the alkanes carbon selectivity increased with and without hydrogen being co-fed to the reactor (see WSBO-HCl-$H_2$ and WSBO-HCl). Low methane selectivity and a fairly even distribution of C2 to C6 alkanes is observed in case of the acidified feed (see Fig. 3 and 4).

## 4.0 Discussion

### 4.1 Proposed reaction system

From the elemental analysis data, the non-hydrogenated WSBO can be represented by a molecular formula $C_2H_{5.4}O_{2.05}$ with an arbitrary molecular weight of about 62. The amount of hydrogen in water soluble bio-oil increases during the hydrogenation step and depends on the hydrogen consumption in this step. About 25% of the carbon is converted to $CH_4$ in the hydrogenation step under current conditions. Clearly, reducing the amount of methane formed in the hydrogenation step is of critical importance in obtaining commercially relevant yields. Methane can form by the hydrogenation of CO produced upon decarbonylation of bio-oil compounds. A mole of water is also formed when a mole of $CH_4$ is obtained from hydrogenation of CO. The hydrogen consumption in this step is about 0.06 g/g WSBO for a reaction temperature and time of 175 °C and 3 h, respectively. For 0.06 g $H_2$ consumed per gram of WSBO, the hydrogenated WSBO can be represented by a molecular formula $C_{1.5}H_{6.1}O_{1.55}$ with a molecular weight of 48.9 (see reaction 4).

$$\underset{\text{Non-hydrogenated WSBO}}{C_2H_{5.4}O_{2.05}} + 1.87\,H_2 \rightarrow \underset{\text{WSBO (or hydrogenated WSBO)}}{C_{1.5}H_{6.1}O_{1.55}} + 0.5\,CH_4 + 0.5\,H_2O \quad (4)$$

Hydrogen is produced by reaction 5 from the bio-oil and water by aqueous-phase reforming. The hydrogen can react with the bio-oil to produce alkanes (pentane is shown as an example), as shown in reaction 6. (No carbon-carbon bond forming reactions are taking place in Reaction 6.) Addition of reaction 5 and 6 so that the hydrogen produced in reaction 5 is consumed in reaction 6, gives reaction 7. From reaction 5 it can be seen that the theoretical highest yield of hydrogen is 0.184 g hydrogen per g of hydrogenated WSBO or 0.145 g hydrogen per g of non-hydrogenated WSBO. The net hydrogen production accounting for hydrogen consumption in hydrogenation step is 0.085 g hydrogen per g non-hydrogenated WSBO. The selectivity of alkanes produced from the water soluble bio-oil depends upon its composition. However, if we assume that pentane is the major product, the theoretical highest yield of pentane that can be produced is 0.326 g per g of non-hydrogenated WSBO (reaction 7).

$$C_{1.5}H_{6.1}O_{1.55} + 1.45\,H_2O \rightarrow 1.5\,CO_2 + 4.5\,H_2 \quad (5)$$

$$C_{1.5}H_{6.1}O_{1.55} + 0.3\,H_2 \rightarrow 1.55\,H_2O + (1.5/5)\,C_5H_{12} \quad (6)$$

$$16\,C_{1.5}H_{6.1}O_{1.55} \rightarrow 1.5\,CO_2 + 21.8\,H_2O + 4.5\,C_5H_{12} \quad (7)$$

In our experiments we were only able to obtain 0.031 g $H_2$ per g of non-hydrogenated WSBO. This is only about 21% of the maximum possible yield (0.145 g). This yield could be

increased by recycling the un-reacted product and decreasing the amount of methane we produce in the low-temperature hydrogenation step. Currently, our hydrogen production in the reforming step is less than our hydrogen consumption in the hydrogenation step. Better reforming catalysts are required to increase the hydrogen production. If higher hydrogen production is achieved, the excess hydrogen produced can be used for the low temperature hydrogenation reaction and to hydrogenate the WIBO. The water insoluble fraction of the bio-oil can be hydrotreated with the hydrogen produced from the aqueous fraction of the bio-oil to produce aromatic fuel. WIBO also has the potential to replace phenol in phenol–formaldehyde resins.[6]



### 4.2 Proposed model bio-oil compounds for the aqueous phase of bio-oil

Bio-oil is a complex mixture of several hundred compounds. Hence a complete chemical analysis of bio-oil is very difficult. In our case we were able to identify only 60% of the carbon in the aqueous fraction of the bio-oil using GC-MS and HPLC. For catalyst and process development, it is important to understand the chemistry involved in the hydrogenation and aqueous phase processing of bio-oil. Various model compound studies should be very helpful in this context. Based on our own bio-oil analysis and the available literature,[1,3,4,7,20,24,26] the following model compounds are suggested for the aqueous phase of bio-oils: levoglucosan, glucose, acetic acid, formic acid, hydroxyacetaldehyde, hydroxyacetone, 2-furanone, furfural and guaiacol. Table 6 shows the recommended composition of a model aqueous-phase of bio-oil. Model compound studies should help us understand how each compound behaves during hydrogenation, reforming and APH/D steps. It should also help to understand the interaction between different components in the bio-oil.

### 4.3 Extraction of bio-oil in water

Bio-oil phase separates readily into an aqueous and non-aqueous phases upon addition of water. The aqueous fraction of bio-oil is easy to handle and process. Water is an ideal solvent for subsequent processing steps. It is inert for hydrogenation and takes part in the liquid phase reactions producing hydrogen and alkanes. The composition of the bio-oil, the storage conditions and storage time are the factors affecting the bio-oil phase separation. Some bio-oils can phase separate during storage without the addition of external water. The extent of separation of bio-oil in the two phases can also depend on the method of addition of water to it.[19] The oak wood bio-oil used in our studies phase separates upon addition of small amount of water. The minimum water to bio-oil ratio required for phase separation was 1 : 4 (weight ratio). The amount of bio-oil extracted in water was independent of the amount of water added, as long as the water to bio-oil ratio was above 1 : 4. This ensures that concentrated aqueous solutions of water soluble bio-oil can be used in our process. However, dilute WSBO solutions were used in our studies primarily because of the lack of large amounts of bio-oil.

**Table 6** Recommended model bio-oil aqueous phase composition

| Component | wt% range |
|---|---|
| Formic acid | 4–8 |
| Acetic acid | 8–12 |
| Hydroxyacetaldehyde | 5–10 |
| Hydroxyacetone | 8–12 |
| Furfural | 2–5 |
| 2-Furanone | 2–5 |
| Glucose | 15–20 |
| Levoglucosan | 15–20 |
| Guaiacol | 4–8 |
| Water | 15–20 |

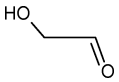
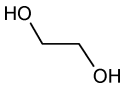
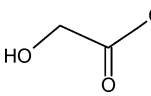
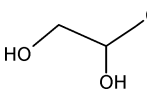
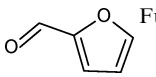
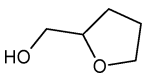
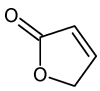
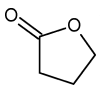
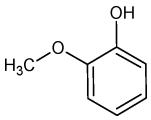
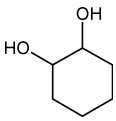
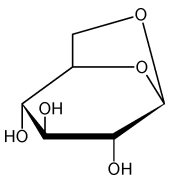
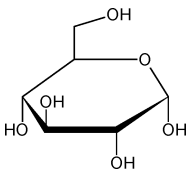
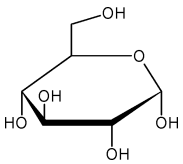
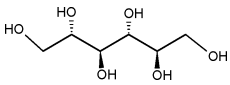
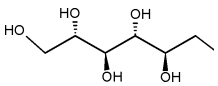
### 4.4 Low temperature hydrogenation of the aqueous fraction of bio-oil

Low temperature hydrogenation makes the aqueous fraction of bio-oil amenable to further processing. Ruthenium on activated carbon was selected, as this catalyst is known to exhibit high activity and stability for similar hydrogenation reactions in the aqueous phase.[27–29] The temperature and reaction time both influence the products that are formed. Optimization of the reaction temperature and time is required, as discussed in Section 3.2. Strong acid (*e.g.* $H_2SO_4$, HCl) can be added to the reaction mixture to increase the rate of acid catalyzed hydrolysis of levoglucosan to glucose. Helle *et al.* showed that increasing the concentration of sulfuric acid increases the rate of hydrolysis of levoglucosan in water at 110 °C.[21]

The hydrogen consumption in this step is up to 0.12 g/g WSBO at 175 °C (Table 3). At high hydrogenation temperature, large amounts of undesired methane is produced. This results in a significant increase in hydrogen consumption during this step. Methane formation also results in reduced hydrogen production in APR.

Based on GC-MS and HPLC analysis of the feed and product of the hydrogenation reaction, the major reactions occurring during this step are identified and are depicted in Table 7. The last reaction in Table 7 is the hydrogenolysis reaction, wherein α,ω-diols are produced from the sugar alcohols such as sorbitol in the presence of hydrogen. Ruthenium metal can catalyze the hydrogenolysis reactions.[30–32] Ruthenium can also catalyze the C–C bond breaking reactions. The relative rates of hydrolysis of C–O bonds and cleavage of C–C bonds decide the final product distribution. Apart from the reaction mentioned in Table 7, decarbonylation and methanation reactions also happen during this step. Another process option is to extract the polyols from the hydrogenated aqueous-fraction of the bio-oil. The three major products after hydrogenation are ethylene glycol, propylene glycol and 1,4-butanediol. We produced 0.102 g ethylene glycol, 0.064 g propylene glycol and 0.021 g 1,4-butanediol per g of non-hydrogenated WSBO. The polyols can be separated from the aqueous fraction either by distillation or nanofiltration. The concentration of the aqueous phase will decide the distillation efficiency. Nanofiltration is an attractive option where molecules can be separated based on size and functionality. The smaller polyols (C2 to C4) can be separated from the hydrogenated aqueous fraction, and be used for the production of hydrogen. Whereas the larger polyols (sugar alcohols) can be used to produce alkanes.

**Table 7** Reactions in hydrogenation of water soluble fraction of bio-oil

| Reactant | Product | Type of reaction |
|---|---|---|
|  Hydroxyacetaldehyde |  Ethylene glycol | Hydrogenation |
|  Hydroxyacetone |  Propylene glycol | Hydrogenation |
|  Furfural |  Tetrahydrofurfuryl alcohol | Hydrogenation |
|  2-Furanone |  γ-Butyrolactone | Hydrogenation |
|  Guaiacol |  1,2-Cyclohexanediol | Hydrogenation |
|  Levoglucosan |  Glucose | Hydrolysis |
|  Glucose |  Sorbitol | Hydrogenation |
|  Sorbitol | Ethylene glycol, propylene glycol and 1,4-butanediol | Hydrogenolysis |

### 4.5 Reforming of the aqueous fraction of bio-oil to produce hydrogen

In this study it is shown that the aqueous-fraction of bio-oil can be converted to hydrogen and alkanes. A process flow diagram that shows how bio-oil could be converted into liquid fuels and chemicals is shown in Fig. 5. Fig. 5 shows mass balances for the different reactions assuming 100% of the theoretical yield and 25% of methane is produced.

In the first step in this process, the bio-oil is mixed with water (1 : 1 weight mixture) and separated into a water soluble fraction (WSBO) and a water insoluble bio-oil (WIBO). Approximately 62 wt% of the initial bio-oil goes into the WSBO and 38 wt% of the initial bio-oil goes into the WIBO. The WSBO is then sent to a low temperature hydrogenation unit where the hydrogen consumption is up to 0.12 g/g bio-oil. In Fig. 5, hydrogen consumption of 0.06 g/g non-hydrogenated WSBO is shown. The purpose of this unit is to stabilize the bio-oils. The hydrogenated WSBO is then sent to an aqueous-phase reformer where hydrogen is produced. The maximum amount of hydrogen that can be produced from 100 kg $h^{-1}$ of bio-oil is 9 kg $h^{-1}$. In the process, 66 kg $h^{-1}$ $CO_2$ and 8 kg $h^{-1}$ of methane will also form. The hydrogen consumption is 3.7 kg $h^{-1}$ in the hydrogenation step. The net hydrogen production for this process is 5.3 kg $h^{-1}$. After the hydrogenation step, the polyols can be separated out if desired. The unreacted bio-oil is re-concentrated and recycled back to the reactor.

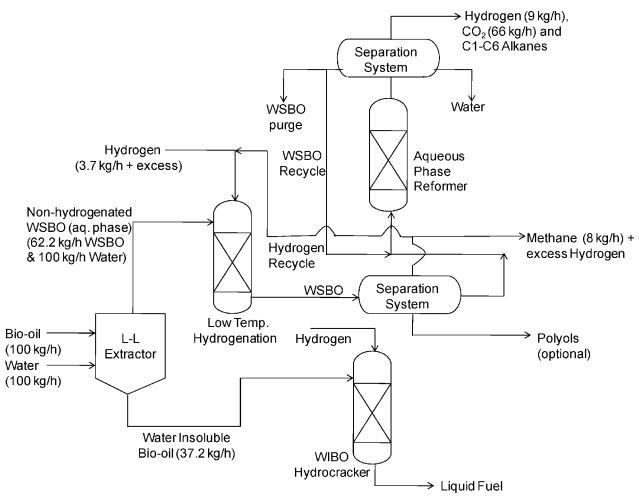



**Fig. 5** Process flow diagram for aqueous phase reforming of bio-oil.

In our experiments, hydrogen is produced from the aqueous fraction of the bio-oil with high selectivity (50–60%). The major challenge is that the bio-oils have low activity. This could be due to poisoning of the catalyst surface by acids or other impurities. Lower hydrogen selectivity is observed for bio-oil (50%) as compared to sorbitol (64%) at similar conversion. Bio-oil exhibits low reforming activity, though with moderate hydrogen selectivity. The moderate hydrogen selectivity can be attributed to the presence of smaller oxygenated hydrocarbons in the aqueous fraction of bio-oil. Smaller oxygenates present in bio-oil are converted to smaller polyols such as ethylene glycol and propylene glycol upon hydrogenation. These polyols can produce hydrogen in high yield as compared to larger polyols, such as sorbitol. These polyols also have higher rates of reaction than sorbitol.[13,15] Even though it contains smaller polyols, the aqueous fraction shows lower hydrogen selectivity as compared to sorbitol. This can be due the presence of unreacted sugars and other unidentified compounds in the aqueous fraction.

Theoretically, about 0.085 g of hydrogen can be produced from a gram of non-hydrogenated WSBO when about 25% of the carbon is converted to methane in the hydrogenation step. We were able to produce 0.031 g of hydrogen from a gram of non-hydrogenated WSBO, while consuming 0.06 g hydrogen in the hydrogenation step. The low hydrogen production is due to two reasons (a) high carbon loss and hence the hydrogen loss to gas phase during hydrogenation and (b) low activity of bio-oil in reforming. About 0.032 g hydrogen per g non-hydrogenated WSBO is lost in the form of methane during hydrogenation at 175 °C. To reduce the carbon loss, optimization of reaction temperature and time is necessary, as discussed earlier. A catalyst with low decarbonylation activity is desired for the hydrogenation step. For reforming, a catalyst with high activity for bio-oil is desired. The low reforming activity seen for $Pt/Al_2O_3$ catalyst can also be due to various impurities in the bio-oil. Effects of the bio-oil impurities (*e.g.* alkali salts of organic acids) on the reforming process needs to be studied. Bi-metallic catalysts are known to be highly active for the reforming of ethylene glycol[15] and can potentially be used for reforming of aqueous fraction of bio-oil.

### 4.6 Liquid phase dehydration/hydrogenation of aqueous fraction of bio-oil

The process flow diagram for the production of alkanes from the aqueous fraction of the bio-oil is shown in Fig. 6. The amount of alkanes produced is shown with 100% carbon conversion to alkanes. The process is essentially the same as that for APR, except that the APR reactor is replaced by the APD/H reactor. Theoretically, when hydrogen is not supplied externally, about 18.0 to 20.4 kg $h^{-1}$ of C1 to C6 alkanes mixture can be produced from 100 kg $h^{-1}$ of bio-oil (62.2 kg $h^{-1}$ non-hydrogenated WSBO). At the same time, 3.5 to 16.0 kg $h^{-1}$ of $CO_2$ and 8 kg $h^{-1}$ of $CH_4$ will be produced. The composition of the alkane mixture produced depends on the composition of WSBO. Hydrogen can be supplied externally to the APD/H reactor to increase the carbon selectivity towards alkanes.

In our experiments, alkanes are produced at modest yields from the aqueous fraction of bio-oil over a bi-functional catalyst.

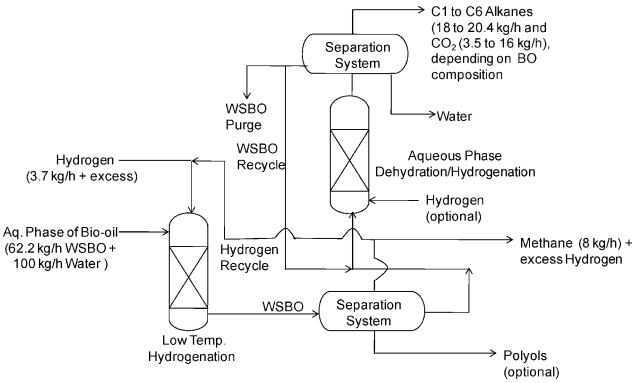



**Fig. 6** Process flow diagram for the aqueous phase dehydration/hydrogenation of bio-oil.

Conversion for bio-oil is almost half of that for sorbitol. From Fig. 6, it can be seen that 0.289 to 0.328 g alkanes can be produced per gram of non-hydrogenated WSBO. We were able to produce up to 0.139 g alkanes per gram of non-hydrogenated WSBO, which is 42–48% of the theoretical yield. The alkane selectivity and the heavier alkane distributions are better for the bio-oil than the sorbitol. The alkane selectivity can be altered by supplying hydrogen externally or by adding a strong acid to the feed. External hydrogen suppresses the C–C bond breaking reactions that produce CO and $CH_4$ as the by-products. The near absence of methane when hydrogen is supplied externally implies that the methane is a result of C–C bond breaking reactions and not of dehydration/hydrogenation reactions of bio-oil components containing a single carbon atom (*e.g.* methanol). The strong acid can act as a dehydration catalyst and hence can expedite the dehydration reactions resulting in higher alkanes selectivity.

The theoretical selectivities for the individual alkanes from WSBO and hydrogenated WSBO can be calculated from the composition shown in Table 3. These theoretical selectivities assume that no carbon–carbon bond cleavage occurs in aqueous-phase dehydration hydrogenation. This provides an upper limit for alkane production by APD/H. In Fig. 7, the theoretical selectivities are compared with the actual selectivities observed for WSBO-E-H2. Theoretically, no methane should be produced from the hydrogenated WSBO but in actuality up to 16% methane selectivity is observed for hydrogenated WSBO (see Fig. 3). This implies the presence of C–C bond cleaving reactions during APD/H. The actual ethane selectivity is lower than the theoretical value, implying that C2 compounds are involved in the production of methane. Propane, butane and pentane selectivities are higher than what is expected theoretically, implying that other than the respective C3, C4 and C5 compounds, these alkanes are also produced from the C6 compounds.

In this study, only smaller alkanes (C1 to C6) are produced from the aqueous fraction of the bio-oil. These alkanes are less valuable as fuel. The aqueous fraction of the bio-oil can essentially be used to produce larger gasoline range alkanes by carrying out some C–C bond formation reactions (*e.g.* aldol condensation) within it, followed by APD/H.[33,34] Presence of various aldehydes and ketones makes the bio-oil aqueous fraction an excellent candidate for such reactions.

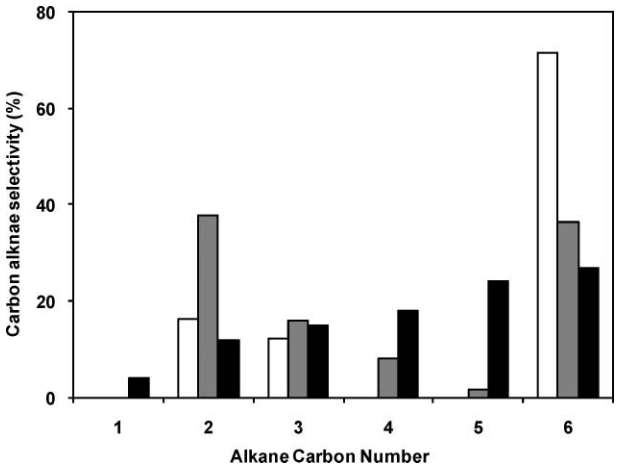



**Fig. 7** Theoretical and actual alkane selectivities for the production of alkanes from the aqueous fraction of the bio-oil. Legend (refer Table 5): (□) non-hydrogenated WSBO – theoretical, (▩) hydrogenated WSBO – theoretical, (■) WSBO-E-$H_2$.

### 4.7 Comparison of aqueous-phase processing of bio-oil to hydrotreating of bio-oil

To date, all the efforts to upgrade bio-oil have revolved around hydrotreating and zeolite upgrading. In hydrotreating, oxygen is removed in the form of water in the presence of a catalyst at high temperature and high hydrogen pressure.[9,10] Baker and Elliott developed a two step process in which bio-oil is subjected to mild hydrotreating at 300 °C and 137.8 bar (total P) to make a stabilized product, followed by further hydrocracking at 350 °C and 137.8 bar.[8] A relatively low LHSV of 0.07 volume of oil per volume of catalyst per h is used in the second step. Sulfided Co-Mo based catalyst was used in both the steps. About 75% carbon is converted to the oil phase containing 2.3 wt% oxygen. Hydrogen consumption is about 0.034 g/g of bio-oil. The advantage of this bio-oil upgrading approach is that all the reactions appear in one single step. The advantage of our approach is that we process the aqueous phase of the bio-oil differently than the organic phase. The aqueous phase is significantly different in composition than the organic phase. This allows us to design catalysts that are well suited for conversion of both the aqueous and organic phases. We believe that in the future this will allow us to achieve higher overall yields for conversion of bio-oils into liquid fuels and chemicals. It would be advantageous to separate smaller molecules from the bio-oil prior to hydrotreating, especially since these molecules form lighter gases during hydrotreating. These smaller molecules could then be sold as chemicals or reformed to hydrogen. Bio-oil composition changes depending on the feedstock. We envision that our process can handle any type of bio-oil. All the small aldehyde and ketonic functionalities in the aqueous fraction will be converted to corresponding polyols. These small polyols are excellent feedstock for the production of hydrogen and alkanes. The challenge would be converting all types of sugars and anhydrosugars to corresponding alcohols. Strong acid may need to be added in the hydrogenation step to facilitate hydrolysis of anhydrosugars to corresponding sugars. Another challenge would be processing bio-oils with high ash content. The Na, K, Ca and Mg salts in the ash can end up in the aqueous fraction and can de-activate the APP catalyst.

## 5.0 Conclusion

The general conclusion from this study is that hydrogen and alkanes can be produced from the aqueous fraction of bio-oil by aqueous phase processing. Thus, previous work on aqueous phase processing of model biomass compounds[12,13,33] can be applied to processing of feedstocks derived from lignocellulosic biomass. This thus offers a new concept for the conversion of lignocellulosic biomass into fuels and chemicals.

The first step in this process is to add water to the bio-oil and separate it into aqueous and organic phases. The aqueous phase is then sent to a low temperature hydrogenation unit where thermally unstable functionalities are hydrogenated to thermally stable compounds. In this hydrogenation step aldehydes are converted to alcohols, sugars to sugar alcohols, and aromatics are hydrogenated. Undesired methane is also formed from this reaction. A key need in this low temperature step is to reduce the amount of hydrogen that is consumed.

Hydrogen is produced at a hydrogen selectivity of 60% from the water soluble part of bio-oil. This selectivity is comparable to that observed for pure sorbitol at similar conversions. This makes bio-oil a feasible feedstock for the production of hydrogen. We have demonstrated here the feasibility to produce hydrogen from the water soluble bio-oil, but future research is needed to determine how the carbon conversion to gas phase can be increased maintaining the high selectivity. Concerns about catalyst stability must also be answered to efficiently use aqueous phase processing.

Alkanes are produced from the water soluble bio-oil by aqueous-phase dehydration/hydrogenation with a bifunctional catalyst. An alkane selectivity of 77% is obtained when hydrogen is co-fed with the bio-oil. Alternatively, an alkane selectivity of 45% is obtained when hydrogen is produced *in situ* from the bio-oil itself. The $C_5$ plus $C_6$ carbon selectivity ranges from 35 to 76% depending on the process conditions.

For these reactions to become an industrial process the overall yield must be increased. Catalyst deactivation problems must be overcome and a more active catalyst must be developed. However, in spite of these current difficulties it is highly likely that more efficient catalytic processes will be developed for the conversion of pyrolysis oils into fuels and chemicals as we continue to understand the chemistry of this process and develop new generations of catalysts.

## Acknowledgements

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