Direct Catalytic Upgrading of Biomass Pyrolysis Vapors by a Dual Function Ru/TiO_2 Catalyst

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The results of catalytic treatment of vapors exiting a g/min pyrolysis unit before product condensation to the liquid phase using a Ru/TiO_2 catalyst for oak and switchgrass pyrolysis are reported. The pyrolysis is conducted at 500°C and the catalysis at 400°C at atmospheric pressure with a hydrogen partial pressure of 0.58 atm. It is found that the catalytic treatment provides significant conversion of light oxygenates to larger, less oxygenated, molecules and, simultaneously, bio-oil phenolics are also converted to less oxygenated phenolics with methoxy methyl groups transferred to the ring. The activity of the catalyst gradually diminished with increasing biomass fed to the system. Untreated pyrolysis oil forms a single liquid phase with some tarry material, consistent with the literature, whereas the treated liquid product forms separate oil and aqueous phases, the latter of which is about 80% water. The oil from the treated vapors has a lower initial viscosity with only a small increase upon accelerated aging compared to the untreated product oil, which has a dramatic increase in viscosity after aging. This is indicative of poor oil stability for untreated oil that is further confirmed by large increases in molecular weight, while the treated oil has a small increase in molecular weight after accelerated aging. In an effort to understand compatibility with refinery streams, the solubility of the oils in tetralin was examined. The untreated oil was found to have very limited solubility in tetralin, whereas the treated oil phase was completely soluble except for a small aqueous phase that appeared. There are a number of challenges in developing a high yield process for pyrolysis based conversion of biomass to transportation fuels. The Ru/TiO_2 catalyst used here shows promise for conducting multiple types of favorable reactions in the presence of the full spectrum of primary pyrolysis products that creates significant product stability under mild conditions. This could lead to higher liquid yields of stable, refinery compatible, product oil. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 2275–2285, 2013

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Introduction

Fast pyrolysis, where biomass is exposed to high temperatures (usually about 500°C) at a high heating rate in an inert atmosphere, has been cited as the lowest cost pathway to convert the polymeric cellulose, hemicellulose, and lignin into smaller, liquid molecular weight range molecules to produce fuels.[1–3] Liquid yields of up to about 70% of the biomass can be achieved, with the remainder converted to biochar and gases (primarily CO and CO_2). The elemental composition of the liquid range pyrolysis oil is only slightly different than that of the parent biomass. A small amount of deoxygenation occurs through formation of CO, CO_2, and water, so carbon is lost at a relatively similar rate through formation of the carbon oxides and bio-char. The liquid pyrolysis oil consists of hundreds of different molecules nearly all of which remain oxygenated. These molecules include the products of carbohydrate depolymerization and fragmentation which can include monomeric dehydrated sugars (i.e., levoglucosan), various furans (C_5—C_8), and light oxygenates ($\leq C_4$, including acetic acid, hydroxyacetaldehyde, acetol, and C_2—C_4 ketones and aldehydes).[4] These light oxygenates represent as much as 15–25% of the biomass carbon, depending on pyrolysis conditions and biomass pretreatment. The pyrolytic depolymerization of the lignin fraction produces a mixture of phenolics most of which are substituted with methoxy groups at the 2 and/or 6 positions. In addition to the C_6—C_{12} monomeric phenolic units, the pyrolysis oil can contain about 25% phenolic oligomers most of which are dimers, trimers, and tetramers; however, molecules as large as 5000 Da can be present.[5,6] These lignin fragments are a large contributor to the high viscosity of condensed pyrolysis oil.

The pyrolysis oil is highly corrosive, with relatively low heating value and combustion properties and with many reactive oxygen moieties, and it tends to polymerize upon storage, making it more difficult to transport and to refine. Thus, it is unsuitable to use as a refined blendstock, and it is poorly suited for a refinery feedstock.

To convert biomass to fungible fuels or refinery blendstocks, biomass oxygen must be substantially removed. At the same time, the hydrogen to carbon ratio of the biomass

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is also somewhat low. There is no real single chemical pathway to achieve this objective and any practical conversion will be a combination of several that involve loss of H_2O and CO_2 in addition to other reactions that are less efficient, for example, loss of CO and loss of smaller hydrocarbons, such as light alkanes or alkenes, as well as small oxygenates (acids, aldehydes, etc.). Additionally, with the loss of water and low H/C ratio of the resultant products, hydrogen will need to be added. The major problem is how to do this while meeting the requirements of low cost and environmental impact, and also maximizing fuel (or chemicals feedstocks) production. There is not likely to be one single process that will satisfy all of these requirements, for any feedstock, in any location, but there is one overarching point that should be recognized. The primary goal of making investments in biofuel/biorefinery processes (and the full value chain that includes growing the biomass) is, ultimately, to displace fossil resources. Within all of the constraints that must be satisfied to be successful then, is the yield of biofuel (or bio-chemicals) that displaces petroleum. The potential of these biofuel solutions is limited to the amount of biomass that can be converted. According to the USDA-DOE Billion ton study,[7] this would be on the order of one billion tons per year, without displacing food crops. Thus, once some biomass carbon is lost from the desired product stream (liquid fuel components), more feedstock cannot be obtained arbitrarily. Note that this is true on a plant by plant basis in that one cannot build a plant based upon the assumption that biomass feedstocks can be obtained from any distance; so for any plant, the maximum practical distance from which feedstocks may be transported will govern the process size, not the output of the final product or maximizing the economy of scale. Thus, for a similar investment and similar acreage, the product yield obtained is a critically important variable for economics and petroleum displacement. An improvement in yield translates directly to reduction in capital and operating costs per unit of production.

Most processes under development for catalytically upgrading pyrolysis products generally involve two catalytic functions, acids such as zeolites and/or hydrotreating at high pressures over metal-based materials. The process configurations are varied and include use of catalysts within the pyrolyzer;[8,9] (less commonly) use of catalysts following the pyrolyzer operating in the vapor phase;[10–12] and, predominantly, collecting the products as a liquid (pyrolysis oil) and then hydrotreating in an essentially separate unit operating at high pressure.[13,14] Virtually, all configurations incorporate this last step.

Acidic catalysts used for this upgrading include a wide variety of materials, but most common are zeolites. The number of zeolites that have been tested for this application is large and the zeolites have included many additives including alkali, rare earth, and noble metals. Investigations go back at least to the 1980s when the crystalline zeolites became widely available.[15,16] HZSM 5 still seems to be the most useful catalyst,[17] but larger pore Y and related FCC type materials are also used. With HZSM 5 especially, aromatics are a significant target product, produced primarily from dehydration of carbohydrate derived precursors. One of the issues is that biomass pyrolysis conditions may not be suitable for *in situ* zeolite upgrading, wherein the temperature of the catalysis must be the same as the pyrolysis, which may not be optimal. At these conditions of high temperature, many smaller fragments may be produced which leave the reactor mostly as light olefins (with further loss of liquid yield). These olefins might then be recovered by oligomerization in a separate step after separation.[8] Coke formation on the zeolite is typically significant and decreases the carbon yield in the liquid product, although the coke (and char) may be burned during regeneration to supply the heat needed for the system. The coke causes rapid catalyst deactivation necessitating large catalyst to oil ratios and almost certainly continuous regeneration in something similar to an FCC type configuration. Additionally, the char/coke combustion may require additional catalysts to convert CO and the high temperatures and presence of the high partial pressures of water may significantly reduce catalyst (replacement) lifetime even with ultrastable versions of the catalyst (in the case of the larger pore materials). Obtaining hydrogen from this carbon also appears to discount the loss of liquid product yield and the low yield of hydrogen per carbon compared to natural gas, thereby increasing net CO_2 production[18] and possibly capital cost if a separate reformer is required.

The other major avenue for upgrading the pyrolysis oil is hydrotreating. Two proposed configurations are (1) hydrotreating after condensing the liquid bio-oil[13,14] and (2) by high pressure pyrolysis with hydrotreating in the pyrolysis reactor, followed by high pressure hydrotreating.[19] In both configurations, hydrotreating is typically multiple stages with different, but high pressure, operating conditions. The oxygen is removed as water, but the small oxygenates leave as light alkanes, methane, ethane, propane, and so on. The loss of this carbon greatly reduces liquid yield (lost liquid yield of 15–25 wt % of the original biomass, depending on feedstock). At the same time, substantial hydrogen is carried away in the light alkane products. The hydrogen may be mostly recoverable by reforming the alkanes product gas stream, but as mentioned earlier, this loss of carbon yield in the liquid has significant impacts on the net CO_2 reduction (since less petroleum transportation fuel is displaced) and the reforming is likely less efficient (in terms of direct CO_2 production) than methane steam reforming.

For the final use of the pyrolysis oil as a transportation fuel, compatibility with existing fuels is the goal. Cost effectiveness suggests that the upgrading/refining conducted on the small scale with the pyrolysis should be minimized in favor of larger scale refining at consolidated sites, such as an existing petroleum refinery. Thus, the goal of distributed upgrading would be to stabilize the oil to prevent degradation of properties and also to produce a product that will be compatible with insertion points of existing refineries. While stabilization criteria are relatively well known, for example, limited change in viscosity with storage for one, compatibility with petroleum refinery streams is more difficult to determine. What will the refiners accept? Christensen et al.[20] studied the extent of conversion of the various oxygen groups in distillate fractions by hydrotreating at various levels of severity, but the severity levels needed by refiners are not defined. Mercader et al.[21] have performed studies considering these issues and offer some guidance on critical parameters. Among the important issues are solubility in the petroleum derived stream as well as tendency to coke.

As an alternative, an upgrading strategy to minimize the loss of carbon while stabilizing the oil before further treatment may be considered. Various configurations may be envisioned, but we describe here the conversion of the pyrolysis vapors before their condensation to liquid pyrolysis bio-oil. Several types of chemistry may be used depending on

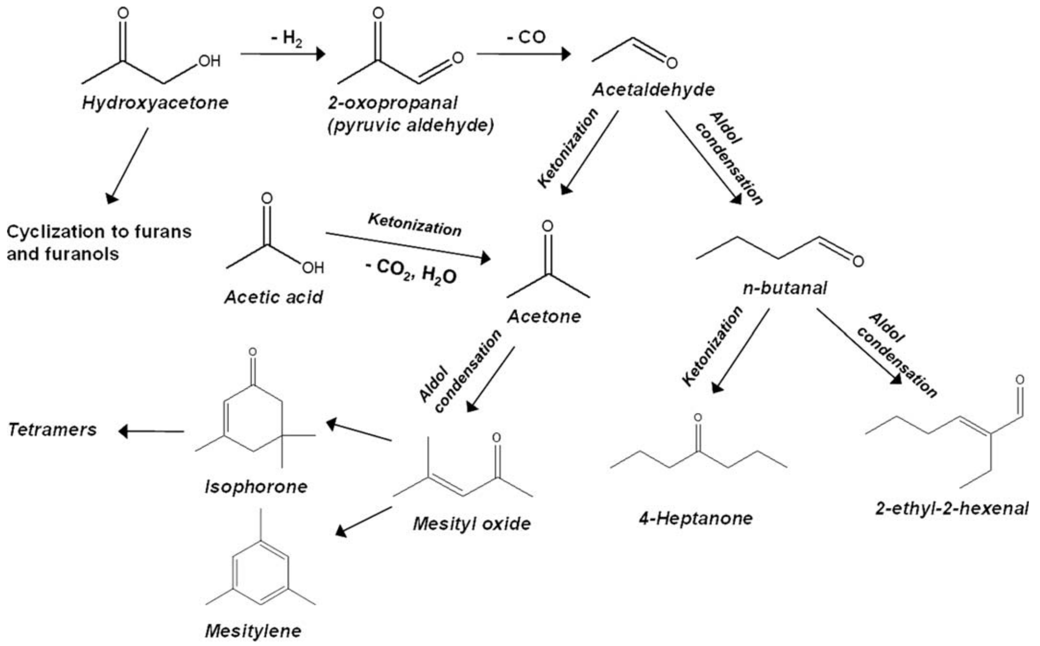

Figure 1. Condensation reaction pathways for bio-oil light oxygenates based on model compound studies over a metal oxide catalyst.

the target molecules, including light oxygenate condensation reactions and mild deoxygenation with transalkylation.

Approximately 40–60% of the carbon in nonupgraded bio-oil is in the category of light oxygenates containing four or fewer carbons. Most of this carbon would be lost from the liquid product with the approaches discussed earlier, so retaining this carbon during upgrading can represent a major improvement in overall carbon capture in the liquid product. The pathway (Figure 1) shows the condensation pathways of the light oxygenates over oxide catalysts, consisting predominantly of aldol condensation and ketonization reactions at moderate temperatures. The utility of these reactions is that carbon chain number is significantly increased while oxygen, particularly reactive oxygen, is reduced and no hydrogen is consumed. These reactions have been studied extensively on model systems and make use of acid and/or base properties of zeolites and metal oxides (some of which also make use of oxygen vacancies).[22–31] ZrO_2 suppresses ketonization and its loss of carbon compared with CeO_2 and their mixed oxides, but still allows conversion of acetol and acetic acid.[32] The analogous conversion pathways exist for the other pyrolysis products in this category, such as acetone, acetaldehyde, furfurals, and so on.

The lignin fraction can vary greatly from as low as 10% for switchgrass to 40+% for some woody biomass. The resulting phenolics product fraction include methoxy groups that represent 10–15% of this carbon and is typically lost upon cracking and hydrotreating, reducing alkylaromatics and increasing benzene yield. Overall carbon yield could be increased perhaps 10% by retaining this carbon by transalkylation of methyl groups to the ring, with substantially improved fuel quality. Additionally, the phenolics are typically multifunctional, with more than one oxygen. As mentioned earlier, these multioxygenated phenolics are a key component of the high molecular weight materials that polymerize in the liquid phase. It has been shown[33] that these oligomers from lignin pyrolysis form after condensation and do not appear to be a significant product in the pyrolysis vapor, where mainly phenolic monomers are observed, also confirming much earlier work on primary products from pyrolysis by Evans and Milne.[34] We have recently shown that acidic zeolite catalysts can be used to retain methoxy carbon by transalkylation of the methoxy methyl group to the aromatic ring, reducing methane production.[35–37] Additionally, under atmospheric pressure hydrogen, the incorporation of a metal in the zeolite catalyzes deoxygenation without hydrogenation of the aromatic ring. Further work has shown that guaiacol, due to its two oxygen groups, is much more deactivating than anisole. Nevertheless, good activity for converting guaiacol for both transalkylation and deoxygenation has been found for metal/metal oxide dual function catalysts, with Ru/TiO_2 showing the best results thus far, although the deoxygenation function is less stable,[38] as shown in Figure 2. With increasing time on stream, guaiacol conversion remains high, but the ability of this catalyst to promote complete deoxygenation decreases, while continuing to remove one oxygen atom. We have found conditions in which stable conversion to mostly cresols, for example, retains the methoxy carbon and the products are much less deactivating. These single oxygen aromatics are ultimately more easily fully deoxygenated under mild hydrotreating conditions, without forming cyclohexanes. In a similar fashion, we have examined the ketonization of acetic acid over a Ru/TiO_2 catalyst, although under different conditions, and found it to be highly effective[39] for this reaction, with further studies on the reactions of light oxygenates ongoing. Efforts to treat the pyrolysis vapors with metal oxide and metal/metal oxide catalysts have been made by Lu et al.[12] and showed the potential for upgrading the vapors coming from the pyrolysis unit.

Thus far, our studies have been applied to model compounds and to simple mixtures to develop understanding of the chemical pathways. In this article, we report results of catalytic treatment of vapors exiting a g/min pyrolysis unit before product condensation to the liquid phase using a Ru/TiO_2 dual function catalyst.

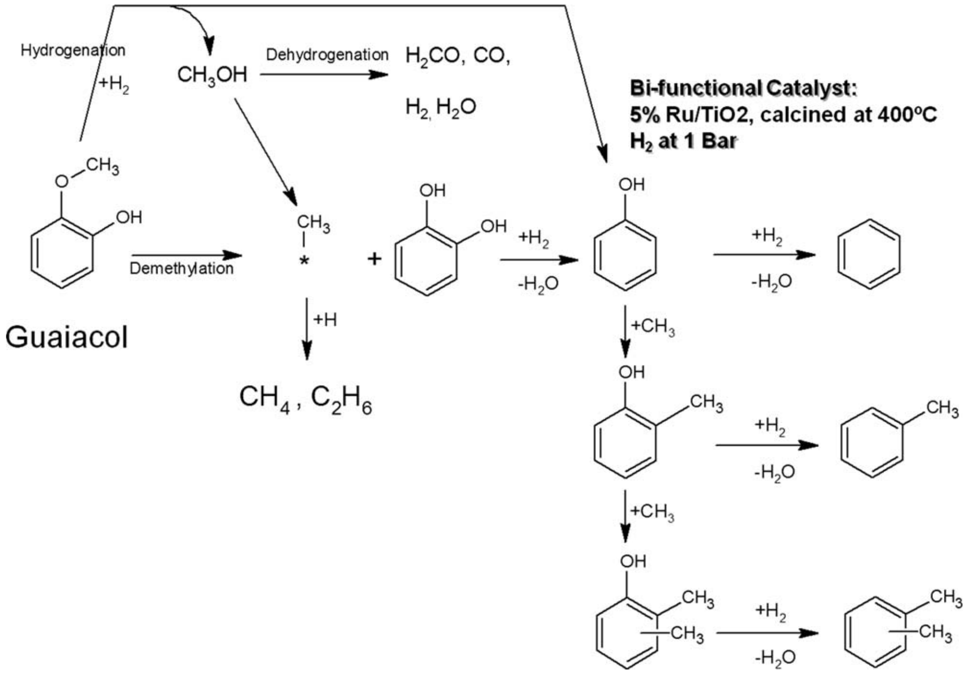

Figure 2. Strategy for upgrading phenolics from bio-oil.

The pathway proposed here is based on phenolic model compound studies using guaiacol over the bifunctional 5% Ru/TiO_2 catalyst.

Materials and Methods

Biomass and catalyst

The feedstocks used in this work were switchgrass and red oak sawdust, both ground to a size of 0.5–1 mm. The ground samples were then dried in vacuum (0.02 MPa) at 60°C overnight and then cooled. The switchgrass was an Alamo variety supplied by the Samuel Roberts Noble Foundation with a lignin, hemicellulose, cellulose, and ash wt % of 9.32, 36.56, 38.65, and 4.87, respectively, based on NIR correlated data. The oak was sourced locally, with an estimated ash content of 2% which was determined by the residue after oxidation at 800°C from TGA experiment. Typical red oak heartwood compositions can be found in the literature with lignin, hemicellulose, and cellulose wt % of 21.3, 46.9, and 27.2, respectively.[40] The dry switchgrass had an elemental composition of 46.0 C%, 6.0 H%, 43.1 O% (O by difference) and oak sawdust of 43.0 C%, 5.8 H%, 49.2 O% (O by difference).

A 5% Ru/TiO_2 catalyst was prepared using the metal oxide, that is, titanium (IV) oxide (Alfa Aesar, Catalyst support, Anatase 1/8″ pellet) with a pore volume of 0.38 cc/g. The oxide was reduced in particle size to smaller than 500 μm, dried overnight (12 h), and cooled to room temperature before the metal impregnation step. The metal was added by incipient wetness impregnation with an aqueous solution of ruthenium (III) chloride hydrate (Aldrich, 99.98% trace metals basis). The ruthenium precursor salt was first dissolved in deionized water in the appropriate amount to obtain 5 wt % of ruthenium metal of the total mass of the catalyst. The prepared precursor solution was added drop-by-drop on the titania with mixing using a glass mortar and pestle. After the impregnation, the catalyst was dried at 120°C for 12 h, and oxidized in flowing air at 400°C for 4 h starting with a heating rate of 10 C/min, and finally cooled to room temperature. The catalyst was pelletized and subsequently crushed and sieved to particles with a size ranging from 450 to 850 μm to minimize the pressure drop when packed into the catalyst bed coupled with the pyrolysis reactor during operation. The detailed synthesis and characterization of the catalyst has been described in model compound studies of Boonyasuwat et al.[38] and Pham et al.[39] The catalyst was then reduced *in situ* as described below.

Bench-scale fast pyrolysis reactor with directly coupled catalyst bed

A continuous bench-scale fast pyrolysis reactor with a flexible capacity of 40–200 g/h biomass was designed, fabricated, and used in this work. This system can allow the addition of selective catalytic stages to upgrade the hot pyrolysis vapor *in situ*. This system is schematically shown in Figure 3.

The pyrolysis reactor was made of a stainless steel tube with an ID of 0.930 in. and length of 12 in. The pyrolysis reactor was externally heated with a one-zone electric furnace, where the actual pyrolysis temperature was monitored by a Type K thermocouple inserted in the center of the reactor tube. The pyrolysis temperature used for these experiments was 500°C. The twin-screw feeder model KT-20 (from KTRON America Pitman, NJ) was controlled by a KTRON digidrive. The dried biomass, preloaded in the feeder hopper, was conveyed by the twin-screw auger into the pyrolysis reactor hot zone through a 1/2″ transport tube. A carrier gas, 0.5 SLPM He, was introduced in the upper part of the transport tube to facilitate the particles' transfer. During the pyrolysis experiment, a flow of H_2 preheated to 500°C was fed from the bottom of the pyrolysis reactor tube at a rate of 0.7 SLPM, which together with the top-fed carrier gas provides an overall gas residence time inside the pyrolysis reactor of 2s. The reactor pressure was just above atmospheric, with a hydrogen partial pressure of about 0.58 atm. The exiting pyrolysis gas–vapor mixture first passed through the cyclone, and then instantly entered the direct-coupled fixed bed catalytic reactor. This was made of a stainless steel

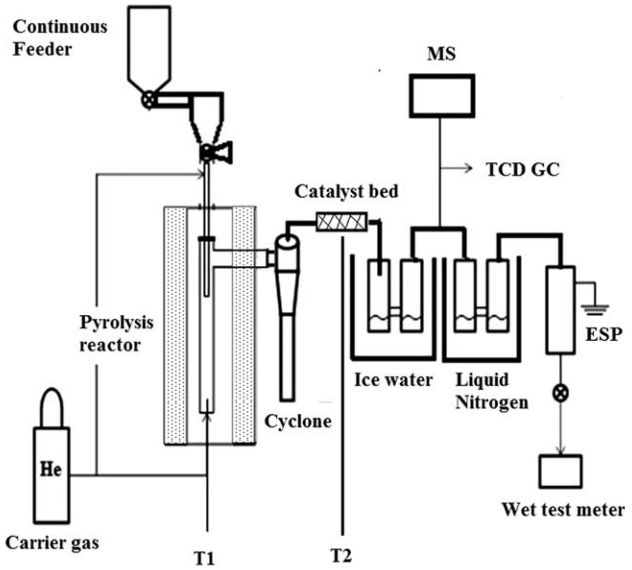

Figure 3. Reactor diagram of bench-scale fast pyrolysis system.

The catalyst bed follows the pyrolysis reactor, directly coupled after the cyclone. The ESP was removed as no product was found to be collected after the train of ice water and liquid nitrogen traps. T1 and T2 refer to the thermocouples that monitor the inside reactor and catalyst bed temperatures, respectively.

tube with an I.D of 0.930 in. and a length of 7 in. The catalytic bed was heated and maintained at 400°C by external heating tapes, where 4–6 g of 5% Ru/TiO_2 was packed in the center and sandwiched by two layers of ceramic wool at both ends. Silica beads were used as a bed for noncatalytic "blank" experiments. The catalyst was reduced *in situ* at 400°C for 2 h before biomass feed was initiated. After the catalyst bed, the upgraded vapor mixture was then condensed by a train of two condensing traps cooled by ice water (trap 1) and liquid nitrogen (trap 2), respectively, where liquid products were accumulated for further analysis. This arrangement allowed online measurement of the gas composition after trap 1 due to condensation of CO_2 in trap 2 during the experiment.

An electrostatic precipitator was initially used, but it collected essentially nothing after trap 2 and was ultimately removed. A wet test meter was used to measure the flow rate for the postcondensation gas mixture, before its release to the vent.

It should be noted that in this system the activity of the catalyst cannot be monitored continuously *in situ* to determine the deactivation at a certain point of operating time (time on stream). The approach used here to assess this is operation as a semibatch process, that is, the biomass is continuously fed into the pyrolysis reactor, while the produced vapor is condensed and accumulated in the two condensers. After operation feeding 20–30 g of biomass, feed was suspended and the traps replaced, upon which biomass feed operation was resumed. During this interval, the gas flows and system temperatures were maintained. The designation of each catalytic run number, for example, 1st, 2nd, and so on refers to the accumulated products from feeding about 20–30 g of biomass. The typical biomass feed rate used in this work is about 40 g/h. The catalyst amount used in this work for oak and switchgrass pyrolysis was 4 and 6 g, respectively, thus corresponding to a catalyst/feed ratio of about 0.1 and 0.15 h^{-1}, somewhat analogous to a cat/oil ratio. This mode of operation then shows, for these "run" increments, the continuing extent of catalytic activity as additional biomass is fed to the system for successive "runs." These increment sizes allowed sufficient collection of liquid product to complete material balance, composition, and property analyses.

The reactor operation in this work is entrained flow, wherein the particles are carried into the pyrolysis reactor by the transport gas as well as gravity and mix with the main carrier moving upwards from the bottom. The feed rate and the flow rates were chosen so that the char formed was not blown out of the reactor during pyrolysis operation. Under this set of conditions, the cyclone did not accumulate solids during pyrolysis operation.

Gas composition analysis

During the pyrolysis operation, the noncondensable gases were quantitatively analyzed by a CARLE® Series 400 AGC equipped with a thermal conductivity detector that was calibrated with gas mixture standards. The gas was sampled after trap 1 about every 15 min via a 30 mL syringe and injected immediately into the GC.

GC-FID, GCMS

GC/MS analysis was performed on a Shimadzu GCMS-QP2010S for qualitatively identifying different species in liquid bio-oil samples using the NIST database. The column used was a DB-1701 (60 m, 0.25 mm ID, 0.25 μm) with a program set at 45°C for 4 min and ramped to 280°C at 3°C/min and held for 20 min. The injector temperature was kept at 250°C with the helium flow rate maintained at 1 mL/min.[41] Bio-oil samples for this analysis were prepared as ~10% solutions in methanol prior to injection.

Combined with the GC-MS analysis, an HP 6890A GC equipped with a flame ionization detector (FID) was used to determine the quantitative compositions of the liquid samples. The same GC column and the same GC conditions as described in the GC-MS analysis earlier were used so that compounds identified by GC-MS would elute at the same retention time and order from the GC-FID as well. Additionally, known compounds were used to validate the MS identifications and retention times for most of the quantified components. About 0.1 μl of neat liquid product sample was injected for these analyses. When there were separate aqueous and organic phases, they were analyzed separately and then summed together to get overall compositions after multiplying by their respective mass fractions (wt % of per biomass feed).

Viscosity

Viscosity was measured by Brookfield DV-Π+ Pro programmable viscometer. A water bath was connected to the viscometer sample cup, with the temperature set at 40°C. Approximately 0.5 ml of sample was placed at the center of the sample cup for each measurement. Each measurement was repeated for each sample and calibration checks were made. Multiple shear rates were measured, however only those at 120 s^{-1} are reported.

Gel permeation chromatography (GPC)

Molecular weights of bio-oil samples were obtained by a Waters GPC system using a Waters styragel HR column with THF as solvent and a flow rate of 1 ml/m using a Waters 515 pumping system with a 717 autosampler. A

CH-30 column heater maintained a 30°C column temperature. Samples were prepared with about a 1 wt % sample in HPLC grade THF and placed in the autosampler tray. For each measurement, the injection volume was 10 μl. Each sample was analyzed twice. Detection was by a Waters 486 tunable absorbance detector with the wavelength set at 254 nm. The UV response was positive over the retention time range for the model compound standards, including the light oxygenates. However, no response calibration was attempted. The GPC column was calibrated using a series of polystyrene standard chemicals with a molecular weight range from 400 to 40,000 and another seven smaller compounds including guaiacol, naphthalene, toluene, furfural, acetol, acetone, and acetic acid were added to extend the calibration's lower end, because a major portion of the biomass liquid products have a molecular weight less than 400 Da.

Water content and elemental analysis

Water content analysis by weight percent of each sample was carried out by TitroLine Karl-Fischer analyzer (TitroLine KF, SCHOTT Instruments) following the standard instrument procedure. Elemental analysis (for Carbon and Hydrogen, with oxygen content by difference) was performed on switchgrass and oak samples, pyrolysis bio-oils and chars, using a CE-440 Elemental analyzer, following their procedures.

Results

Catalytic and noncatalytic pyrolysis of oak sawdust

As mentioned in the experimental section, the liquid products were separated and collected by two traps in series, cooled by ice water (Trap 1) followed by liquid nitrogen (Trap 2). For the noncatalytic pyrolysis runs, liquid phases in both of the two traps appear as homogeneous fluids except that there was always some heavy part that would not pour or pipette, usually termed as "pyrolytic lignin" in the literature, deposited at the bottom in the first trap. This material is completely soluble in THF. After catalytic treatment, the most apparent change is that there is phase separation in both of the traps. The aqueous phase formed in the first trap, which appears to be pale and clear is mainly water and forms the top layer in Trap 1. The oil phase stays at the bottom, which appears much less viscous than the heavy deposits in the first trap from the blank run. The liquid product collected in the second trap also separates into two phases; however, the oil phase is lighter and sits above the lower pale translucent aqueous phase.

Table 1 summarizes the results comparing the blank and the "first" catalytic run using 4 g of 5% Ru/TiO_2. Previous tests showed no effect of the carrier gas composition on the blank pyrolysis run. In one typical blank run, the products yields, on a % of biomass basis, are 7.0% char, 24.3% gas, and 60.2% total liquid. For the catalytic run, a larger amount of gaseous products, about 33%, are produced at the expense of less total liquid yield, 49.9%, which includes an overall oil phase (including those in both Trap 1 and Trap 2) accounting for 25.3 wt % and an aqueous phase of 24.6 wt %. The combined analyses of the aqueous phases (from both traps) contains mostly water, with a content as high as 80%, while the combined oil phases contains mainly oxygenated organic compounds with only 9% water. The total water produced, summed for all phases, is increased from 13.2% in

Table 1. Product Phase Mass Balances of Oak Pyrolysis at 500°C with and without Catalytic Vapor-upgrading on a wt % of Biomass fed Basis

	Noncatalytic, Oak							4 g 5%Ru/TiO_2 1st Run, Oak						
Oak Product	wt %	C%	O%	H%	H_2O%	H/C (dry)*	O/C (dry)	wt %	C%	O%	H%	H_2O%	H/C (dry)	O/C (dry)
Organic phase	60.2 (1.5)†	57.8 (1.5)	60.9 (1.9)	72.4 (4.2)	13.2 (1.3)	1.60 (0.11)	0.59 (0.04)	25.3 (1.6)	36.9 (1.7)	13.6 (1.1)	31.5 (2.8)	2.3 (0.3)	1.21 (0.10)	0.21 (0.03)
Aqueous phase								24.6 (1.8)	4.5 (0.6)	41.3 (2.7)	40.7 (3.9)	19.6 (2.0)	1.92 (0.15)	0.93 (0.05)
Char	7.0	13.0	1.9	3.1				7.0	13.0	1.9	3.1			
Gas	24.3 (1.4)	23.1 (1.3)	28.2 (1.6)	10.0 (0.6)				33.0 (2.8)	30.2 (2.5)	36.7 (3.4)	13.0 (1.0)			
Total	91.5 (1.4)	93.9 (1.6)	91.0 (2.3)	85.5 (4.5)	13.2 (1.3)			89.9 (1.5)	84.6 (2.0)	93.5 (2.5)	88.3 (4.7)	21.9 (1.4)		

*"Dry" refers to the basis with subtraction of the water content in the sample.

†Data are reported as the average of 2 repeat runs and the numbers in parentheses are the standard deviations.

Table 2. The Products of Oak Pyrolysis with and without Catalytic Vapor Upgrading. Summed for all Phases and Calculated on a wt % of Biomass Basis

	Oak Blank	Ru-TiO_2 1st	Ru-TiO_2 3rd
Acetone	0.32 (0.09)[*]	1.62 (0.17)	0.74 (0.15)
Butanone		0.82 (0.12)	0.57 (0.10)
Acetic acid	6.26 (0.67)	0.84 (0.11)	2.42 (0.31)
Acetol	2.42 (0.29)		0.64 (0.14)
2-cyclopenten-1-one		1.51 (0.16)	1.44 (0.14)
Phenol	0.81 (0.15)	1.58 (0.17)	1.27 (0.16)
Levoglucosan	1.75 (0.19)	0.12 (0.04)	1.46 (0.21)
GC eluent Time Fraction[†]			
0–15 min	13.67 (1.55)	7.89 (0.80)	7.55 (0.78)
15–30 min	9.19 (1.00)	5.66 (0.61)	6.98 (0.69)
30–45 min	7.21 (0.70)	8.60 (0.80)	8.41 (0.75)
45–60 min	7.51 (0.77)	5.00 (0.56)	6.46 (0.60)
60 min	3.17 (0.60)	0.80 (0.14)	2.18 (0.22)
Total organic liquid	40.76 (1.68)	27.95 (1.31)	31.58 (1.52)

[*] Data are reported as the average of 2 repeat runs and the numbers in parentheses are the standard deviations.

[†] The compounds in these lumped factions and those individual compounds are identified first by GC-MS. Up to 15 min, are mostly the small oxygenates (acetic acid, acetol, etc.); from 15 to 30 min, mainly furan and pyran derivatives; from 30 to 45 min, light phenolics with one hydroxyl group; in 45–60 min, heavy phenolics with more than one hydroxyl group mostly; 60 min and above, heaviest volatile part, including levoglucosan, other sugars and even some very heavy phenolics.

the blank to 21.9% after catalytic upgrading, with a basis of the weight of oak input. The char amount remains the same, since no change is expected to occur in the pyrolysis itself. The overall mass balances in both blank and catalytic runs are typically about 90%.

The comparisons of selected components with and without catalytic upgrading are summarized in Table 2. These are based on area fractions in the GC-FID analyses, summed for all phases. These include only those compounds sufficiently volatile to elute from the GC. Among them are acetic acid, acetol, and levoglucosan that are significantly reduced, whereas acetone, 2-butanone, 2-cyclopenten-1-one, and phenol (a mono-phenol) show significant increases. Because the liquid includes a complicated mixture of lignin derived phenolics with small amounts of each compound, it's difficult to identify the change of those individual components after catalytic treatment. To overcome this difficulty, and better illustrate the effect of catalytic deoxygenation, the liquid products are assigned to five sequential lumped groups according to their GC elution time range. These reflect relative shifts in the amounts of the products in the lumps. The products in the beginning cut, up to 15 min, are mostly the small oxygenates (acetic acid, acetol, etc.) which are seen to decrease after catalytic upgrading. The subsequent second cut, from 15 to 30 min, containing mainly furan and pyran derivatives, also shows a significant loss of overall weight comparing to the noncatalytic products. Light phenolics with one hydroxyl group will fall into the third cut from 30 to 45 min, which is the only portion showing an increased amount. Heavy phenolics with more than one hydroxyl group will mostly be covered in the forth cut with an elution time range of 45–60 min, while the last cut with 60 min and above consists of the heaviest volatile part, including levoglucosan, other sugars, and even some very heavy phenolics. Both of these cuts are lower after catalytic treatment. The chemistry behind these changes will be discussed later in Discussion section.

Three sequential feed batches were fed over the same catalyst sample to evaluate deactivation of the catalyst. In the subsequent 2nd and 3rd "runs," a phase separation for the liquid products in both traps was observed, indicating that the catalyst was still active after a treatment of the pyrolysis vapors from about 60 g of oak. As seen in Table 2, the compositions of liquid products from the 3rd batch of the catalytic run still show significant differences from those of the blank. However, compared with the 1st run, those products increased by the catalytic treatment, acetone, 2-butanone, and phenol have decreased towards their blank values, whereas those components such as acetic acid, acetol, and levoglucosan have increased towards their blank values. These changes indicate that while the catalyst is not completely deactivated, it has decreased in activity to a significant extent. The spent catalysts after three batches had a mass of 5.0 g from its initial 4.0 g due to the deposition of 1 g coke, representing about 1.7 wt % of the cumulative biomass fed.

The gas compositions, sampled every 15 min by the calibrated Carle-GC, are plotted in Figure 4. CO, CO_2, and CH_4 are the major gas products. All appear to increase when the catalyst is used, and tend to decrease towards the noncatalytic levels as the catalyst deactivates.

Catalytic and noncatalytic pyrolysis of switchgrass

As shown in Table 3, the typical product yields from the noncatalytic switchgrass pyrolysis are 17.0% char, 22.3% gas, and 54.6% total liquid. For the catalytic run, a fixed catalyst bed containing 6 g of 5% Ru/TiO_2 was used to upgrade the pyrolysis vapors. The corresponding liquid and gas yields are 48.1 and 27%, respectively. More water is produced, indicating that reactions are affected by the catalyst. The char amount remains the same, due to the same conditions maintained inside the pyrolysis reactor for all the runs.

Similar to the results for oak, the liquid products from blank switchgrass pyrolysis did not show phase separation, only some heavy part—"pyrolytic lignin," deposited in the first trap. With catalytic upgrading, both traps have separated aqueous phase and oil phases. The Trap 1 oil phase is heavy and forms the bottom layer, whereas the oil phase in the second trap is lighter and stays above the aqueous phase.

The selected components of the liquid products from the blank and catalytic runs are presented in Table 4. From the first run of the catalytic treatment, acetic acid is lowered to

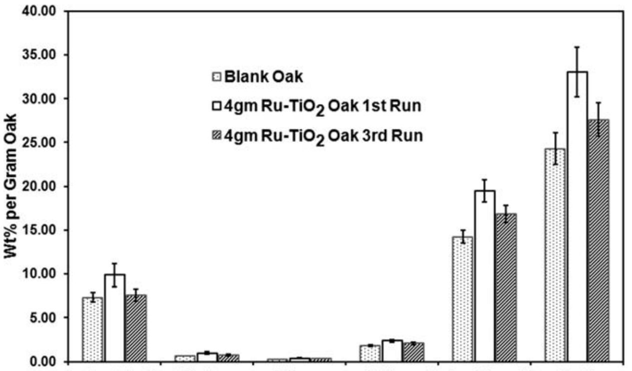

Figure 4. Gas composition from oak noncatalytic and catalytic vapor-upgrading fast pyrolysis where the catalytic 1st and 2nd run refers to the first and second semibatch pyrolysis operation of each sequential feed period of about 30 g of biomass.

Data reported with error bars were averaged from 2 repeat runs.

Table 3. The Products of Switch Grass Pyrolysis with and without Catalytic Vapor-upgrading on a wt % of Biomass fed Basis

	Non-catalytic, Switchgrass					6g 5%Ru/TiO_2 1st run, Switchgrass				
Oak Product	wt %	C %	O %	H %	H_2O%	wt %	C %	O %	H %	H_2O%
Organic phase	54.6	40.5	65.4	70.4	22.6	16.1	23.8	8.4	18.5	1.2
Aqueous phase						32.0	6.0	51.7	57.4	25.4
Char	17.0	26.3	9.3	6.9			26.3	9.3	6.9	
Gas	21.3	21.0	25.0	6.7		28.1	27.0	30.0	11.3	
Total	92.9	87.8	99.7	84.0	22.6	93.2	83.2	99.4	94.2	26.8

0.49%, compared to 1.84% in the blank run products. Acetol drops to an almost negligible level and catechol is hardly seen for the first catalytic run. Dihydro-benzofuran is 1.4% without catalytic upgrading and decreased to about one fifth of that with upgrading. Correspondingly, acetone, one product indicative of ketonization of acetic acid is doubled. Also, a noticeable amount of the completely deoxygenated product toluene is produced as well. Table 4 also lists the compositions of liquid products from the 5th batch of the catalytic run, where the liquid products in both traps still have phase separation. After treating a total of around 125 g of switchgrass, the catalyst remains active for converting acetic acid, catechol, and dihydro-benzofuran. More acetone is produced as well as small amounts of toluene, but acetol is comparable to the level of blank run. This chemistry will be discussed in detail later. About 1.6 gm coke was found to deposit on the spent catalysts after those five runs on the same catalyst sample.

Figure 5 shows the gas composition sampled during the operation by the Carle-GC, where it should be noted that CO_2/CO ratio is much higher than that in oak pyrolysis.

Discussion

Catalytic chemistry

The role of the bio-oil upgrading catalyst used here is not only to eliminate O, but also to retain C in the liquid. Ketonization of acids and transalkylation of phenolic methoxy groups are two desirable reactions readily catalyzed by reducible oxides and acid sites that enhance the C retention, as opposed to HDT catalysts, which convert them to light hydrocarbon gases that consume hydrogen. Deoxygenation is catalyzed by metals. Our group has investigated Ru/C, Ru/TiO_2 (calcined and reduced at different temperature), and TiO_2 catalysts for the conversion of model phenolic and acid compounds. Among them, Ru/TiO_2, calcined at 400°C, shows particularly good activity and stability for the following pathways, demonstrated in Figure 2 above for the model compound—guaiacol:[38]

- Removal of OH groups to form water
- Does not hydrogenate the ring at this temperature
- Retains carbon through methyl transfer reactions
- Converts acetic acid to acetone, for subsequent alkylation or aldol condensation. (As well as condensation of other light oxygenates to higher C less oxygenated species.)

In line with these aspects concluded from the model compound studies, the catalytic effects on the oak/switchgrass pyrolysis vapors will be discussed in detail.

Effects of catalyst

Partial Deoxygenation. Significant amounts of water produced by the catalytic upgrading indicate that the most dominant catalytic reaction to remove oxygen proceeds via dehydration. No guaiacol was found in catalytic switchgrass oil, while an aromatic product like toluene was seen to rise from a negligible amount to 0.15%. However, the total aromatic products including benzene, toluene, and xylene are only a small portion of the overall original phenolics, while phenol is a significant phenolic compound, suggesting that partial deoxygenation is achieved. This is consistent with model compound results show that the single phenolic OH is very resistant to deoxygenation under conditions where ring hydrogenation does not occur, for example, high temperature. No cyclic alkanes are seen, indicating that the phenolic rings were not hydrogenated. A similar trend occurs for the case of oak. Due to a more complicated phenolic mixture from this material, containing greater lignin content, it is difficult to identify the changes to each of component from the catalytic treatment. Alternatively, the lumped product distribution in Table 4 sees the part of 30–45 min grow from 7.21 to 8.60%, where most of the simple phenolics with mono-OH groups will elute. Correspondingly, the 45–60 min elution group, in which mainly heavier phenolics containing multi-OH groups appear, shows a drop from 7.51 to 5.0% after catalytic upgrading. Small amounts of benzene and alkylbenzenes do appear in the catalytically upgraded products. All these clearly show a partial deoxygenation by the catalyst via conversion of multifunctional phenolics to monofunctional phenolics and deoxygenated aromatics under 0.58 atm partial pressure of H_2.

Condensation Reactions. Another significant catalytic effect that is observed is ketonization. Acetic acid was dramatically decreased for both switchgrass and oak, whereas acetone shows a significant increase with catalytic upgrading, as shown in Tables 2 and 4, respectively. Our group's earlier work[29] shows that metal oxides including ZrO_2 and CeO_2 and their mixtures can convert small oxygenates such as acetic acid to acetone and higher carbon number molecules through ketonization and aldol condensation with pathways as shown in Figure 1.

The mixed oxides, such as $Zr_{0.5}Ce_{0.5}O_2$ were found to favor more ketonization due to enhanced vacancy sites at the surface generated via introduction of another metal. The reaction

Table 4. Selected Products from the Switch Grass Pyrolysis Liquid with and without Catalytic Vapor Upgrading, Summed all Phases, and Calculated on a wt % of Biomass Basis

	Acetic acid (%)	Acetone (%)	Acetol (%)	Catechol (%)	Toluene (%)	Dihydro-benzofuran (%)
Blank run	1.84	0.76	1.51	0.80	–	1.48
Catalytic 1st run	0.49	1.47	0.06	–	0.15	0.32
Catalytic 5th run	0.23	1.62	1.13	–	0.06	0.58

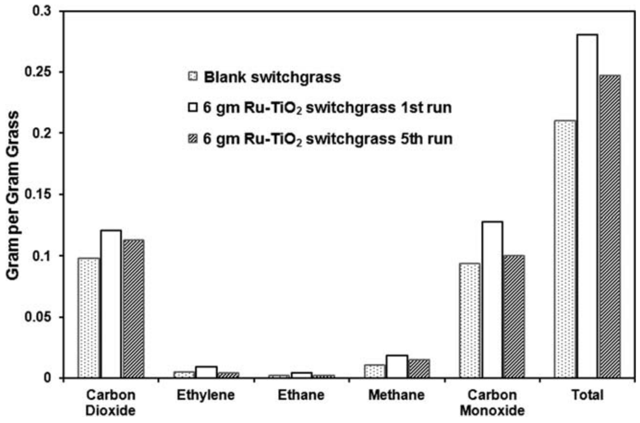

Figure 5. Gas composition from switchgrass noncatalytic and catalytic vapor-upgrading fast pyrolysis where the catalytic 1st and 2nd run refers to the first and second semibatch pyrolysis operation of each sequential feed period of about 30 g of biomass.

pathways on TiO_2 over acetic acid have been explored by several groups.[22,42] As for the bifunctional catalyst in this work (5% Ru/TiO_2), the noble metal not only functions for deoxygenation, but also appears to play a role generating vacancy sites on the TiO_2 surface which promotes ketonization. It should be pointed out that the increase of acetone is not equal to the decreased amount of acetic acid, indicating that other reactions have also contributed to the loss of acid, or that acetone reacts further, as has been shown in model compound studies.

Other small oxygenates also see significant changes. Among them, acetol is almost totally converted, in contrast with a blank value of 1.51 and 2.42% for switchgrass and oak, respectively. Dihydro-benzofuran is another component seeing a sharp drop from 1.48 to 0.32% in switchgrass oil, shown in Table 2.

Overall catalytic effect on oil properties

To provide an overall understanding of the catalytic effects on the pyrolysis oil properties, the oil product elemental composition from oak pyrolysis is shown on a Van Krevelen diagram and stability, and compatibility tests have been conducted for the oak oil samples.

Van Krevelen Diagram. Based on the elemental analysis and water content measured, the H/C and H/O can be calculated on a water free basis for the liquid products. Figure 6 shows the Van Krevelen diagram of those products for both blank and catalytic oak runs, where the oak feed, oak char, and three liquid products points are added following Kleinert and Barth's work.[43] For blank oak runs, the overall liquid products including both trap 1 and trap 2 oil have an O/C ratio around 0.59, and a H/C ratio about 1.60. After catalytic treatment, the O/C and H/C ratio for the combined aqueous phase rises to 0.93 and 1.92, respectively. The combined oil phases see a much lower O/C ratio at 0.22, and also a somewhat reduced H/C ratio at 1.25. The simultaneous decrease for both O/C and H/C indicates that dehydration is a significant pathway for deoxygenation, along with the increased gas yield producing additional CO and CO_2. It should be noted that the carbon content in the aqueous phase only consists of 4.5 wt % of the total biomass carbon, where most of the polar oxygenates such as acids, aldehydes, and levoglucosan appear.

The phase separation following the catalytic treatment is probably attributed to two major factors: dehydration resulting in more water, as well as changes due to conversion of highly polar oxygenates to less polar products. This in itself is a significant improvement in oil quality and allows consideration of further upgrading for the separate phases, and potentially eliminates the need to transport substantial water with the desirable oil product.

Aging and Stability. To evaluate the stability of the oil product, an accelerated aging test was used. This procedure follows the work of Diebold and Czernik[44] and is an empirical method developed by the Department of Energy as a way of characterizing the relative stability of bio-oils produced under different conditions. The liquid sample was aged for 24 h in an oven held at 90°C, with viscosity and molecular weight distributions measured by viscometer and GPC, respectively, before and after aging. Here, the oil phase collected in trap 2 from a blank oak pyrolysis and the first catalytic run have been analyzed and compared. Comparing the blank and catalytically treated oil before aging shows that the treated oil has considerably improved initial properties, with lower viscosity and lower molecular weight, as shown in Table 5. After aging, the oil from the blank run shows significant increases for both viscosity and the average molecular weight, consistent with the literature. The oil from the catalytic run had a comparable initial average molecular weight, but a much lower initial viscosity than that from the blank run. The GPC spectrum, shown in Figure 7, clearly shows a large shift toward higher MW for the blank oil after aging. However, the curve for the liquid from the catalytic run shows only a small change. These results indicate that the liquid products from the catalytic vapor upgrading have much improved stability compared with those from blank pyrolysis.

Compatibility Test. A significant component of ongoing research is trying to develop coprocessing of bio-oil and fossil fuels feeds to conventional petroleum refining units, which can take advantage of the current existing infrastructure such as FCC, HDS, and so on.[21,45] However, to be able to blend with the fossil fuel feedstocks to undertake the subsequent coprocessing successfully, the current conventional approach is high

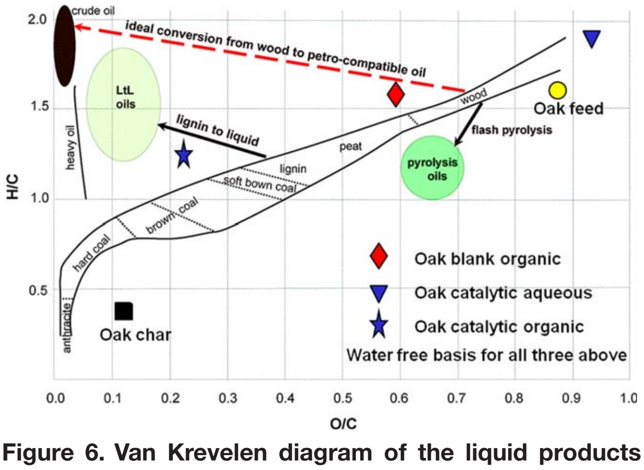

Figure 6. Van Krevelen diagram of the liquid products for both oak blank and catalytic vapor-upgrading pyrolysis.

For blank oak runs, the overall liquid products, including both trap 1 and trap 2 oil. After catalytic treatment, the O/C and H/C ratio for the combined aqueous phase rises to 0.93 and 1.92, respectively. The combined oil phases see a much lower O/C ratio of 0.22, and also a somewhat reduced H/C ratio at 1.25. Following.[43] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 5. Viscosity and Molecular Weight Change Before and after Aging for Oak Pyrolysis Oil

Sample name	Viscosity (cp) at $t = 0$ h	Viscosity (cp) at $t = 24$ h	Water% at $t = 0$ h	Water% at $t = 24$ h	MW at $t = 0$ h	MW at $t = 24$ h
Oak blank	16.1	47.0	14.4%	16.4%	178	297
Oak Ru/TiO_2 1st run	0.5	4.4	10.2%	10.9%	141	150

The liquid samples were aged for 24 h in an oven held at 90°C, with viscosity and molecular weight distributions measured by viscometer and GPC, respectively, before and after aging. The sample from the catalytic run is the organic phase.

pressure hydrotreating, to upgrade the pyrolysis oils first, which may be very costly. As discussed in the previous section, the liquid oil from the direct coupled catalytic treatment has a lower oxygen content and much better stability compared with the blank oil. The question then arises how compatible this oil would be with refinery fractions of crude oil for insertion with feeds in standard industry refining units, such as light cycle oil (LCO). LCO is not a readily available material and has properties that may vary from refinery to refinery and the crude from which it was derived. As an alternative, in this work, tetralin is used as an empirical compatibility model for solubility as it is a hydrocarbon and has both aromatic and naphthenic properties. The test is simply adding together the bio-oil sample with tetralin with a volume ratio of 1:4 in a polyolefin tube at room temperature, sonication for 1 h and then resting to allow phase separation to check the solubility of the bio-oil sample in tetralin. The oil samples used here were from the same sources as those for accelerated aging tests, for example, fresh oil samples. Figure 8 shows that after sonication, the blank pyrolysis oil still has a distinct phase boundary with tetralin on top, and the pyrolysis oil volume was not appreciably decreased. The tetralin phase remained clear with a yellowish tint, indicating that relatively little of the noncatalytic bio-oil dissolved in the tetralin. The liquid oil from the catalytic treatment, however, appears to form a homogenous phase with tetralin in the tube, with only a small amount of clear brownish tinted aqueous phase deposited at the bottom, approximately corresponding to the 10 wt % water content in the oil sample. While this is only an empirical qualitative assessment of compatibility, it nevertheless shows that the catalytically treated bio-oil is significantly upgraded and stabilized, with some loss of yield at very mild conditions.

Conclusions

There are a number of challenges in developing a high yield process for pyrolysis based conversion of biomass to transportation fuels. In this work, conversion of the pyrolysis vapors from two biomass feedstocks has shown that multiple catalytic chemistries result in significantly improved product quality with the potential for retaining more of the biomass carbon in the stabilized liquid product. The chemistry conducted by the Ru/TiO_2 catalyst used here shows promise for conducting multiple types of favorable reactions in the presence of the full spectrum of primary pyrolysis products with stability under mild conditions. Further specification of the criteria for refinery compatibility will be needed to determine the extent of processing that is needed to meet the requirements for both stabilization and refinery insertion to maximize the liquid product yield and reduce the cost of processing.

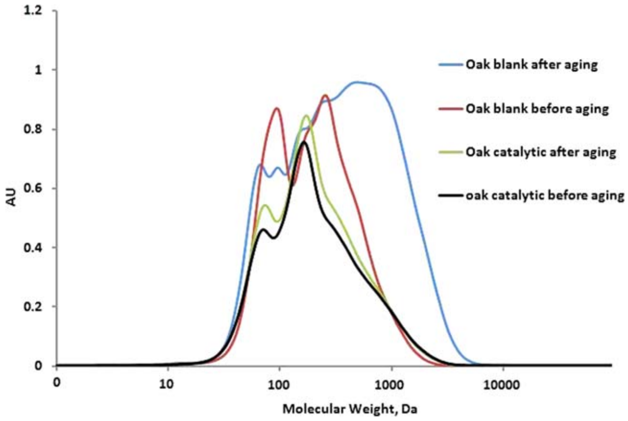

Figure 7. GPC derived MW curves for both oak blank and catalytic vapor-upgrading liquid products before and after aging, during which the liquid sample was aged for 24 h in an oven held at 90°C.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. Compatibility test with tetralin for oak blank and catalytic vapor-upgrading liquid products.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Acknowledgments

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