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Pyrolysis Oil Properties and Chemistry Related to Process and Upgrade Conditions for Pipeline Shipment

January 2012

Prepared by

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Fuels, Engines, and Emissions Research Center

PYROLYSIS OIL PROPERTIES AND CHEMISTRY RELATED TO PROCESS AND UPGRADE CONDITIONS FOR PIPELINE SHIPMENT

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ABSTRACT

Although pyrolysis oil offers a promising way to utilize lignocellulosic biomass for transportation fuel, there are still many challenges associated with its production and processing. This study considers the possibility of transporting pyrolysis oil by pipeline and reviews the logistical and technical challenges associated with this transportation. Pipeline transportation requires that pyrolysis conversion facilities be located near both biomass and pipeline resources, and also that pyrolysis oil be of sufficient quality to not damage pipelines or contaminate the crude oil that is also shipped through these pipelines. In this study, a database on pyrolysis oil processing conditions, physical and chemical properties, and upgrading processes was compiled from published literature. This database was used to model relationships between processing and upgrading conditions and physical and chemical properties. Physical and chemical property data was also compared to data on crude oils and to pipeline operating specifications. Pipeline locations and county-level projections of biomass resources were also compared to address logistical questions about the adjacency of biomass and pipeline resources. It was determined that two-step hydrotreating processes provide the highest level of upgrading, and depending on process conditions, can produce pyrolysis oils that are compatible with crude and might be candidates for pipeline transportation. For this study, we consider pyrolysis oils with less than 2% combined oxygen and water to be candidates for pipeline transportation because these oils also meet requirements for viscosity, gravity, acid content, and crude compatibility. The two-step hydrotreating processes that upgrade oils the most are hydrogen intensive and have low yield. More economic processes significantly improve pyrolysis oil quality but fail to produce oils with oxygen and water content below 2% and fail to meet other pipeline requirements. Analysis of biomass and pipeline resource locations has shown that in 2012 only 7.4% of biomass resources could be utilized under the model of pipeline shipment of pyrolysis oil proposed in this study. However, 18% of biomass resources are projected to be accessible under this model in 2030 because of intensive energy crop development. Hence, if pyrolysis process and upgrading technology continues to improve to the point that pyrolysis oils with oxygen and water contents of less than 2% are economically viable, transportation of pyrolysis oil by existing pipelines could play a significant, but incomplete, role in biomass utilization.

1. BACKGROUND

1.1 INTRODUCTION

Pyrolysis oil is created when biomass is pyrolyzed, or heated quickly in the absence of oxygen. The pyrolysis process produces solids, light gases, and vapors. Solids are removed in a cyclone, and vapors are condensed to form a mix of oil and water. A diagram of this process can be seen in Fig. 1. Although the oil is the desired product of this process, both solids and gases can be burned for process heat. Additionally, the solid product, known as biochar, may be a valuable soil amendment, and the light gases could potentially be used for Fischer-Tropsch processes. Current pyrolysis processes have achieved liquid yields of up to 75 wt %. Unfortunately, the oil produced has poor quality and requires upgrading before it can be considered as a transportation fuel.

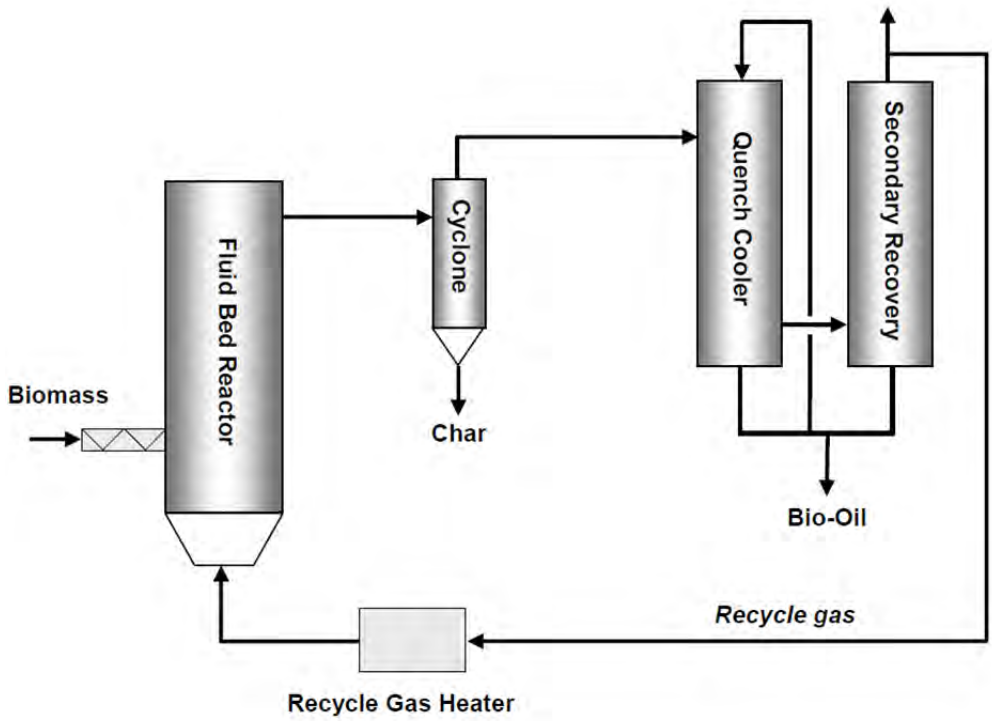

Fig. 1. Diagram of pyrolysis process (9).

Pyrolysis oil has many advantages over traditional biofuels like ethanol and biodiesel. First, it can be produced from any biomass source, unlike ethanol, which relies on crops that store sugar, and biodiesel, which relies on crops that store fatty acids. This means that economic and environmental feedstock costs for pyrolysis oil are likely to be significantly lower than feedstock costs for other biofuels, and that pyrolysis oil feedstocks are unlikely to compete with food crops. Additionally, the pyrolysis process converts lignin, hemicellulose, cellulose, and extractives, while ethanol and biodiesel processes convert a smaller portion of the biomass inputs. Further, the initial pyrolysis process is less complex and less expensive than other conversion processes. Unfortunately, the produced oil is much more corrosive, acidic, dense, and viscous than other fuels. It also is highly contaminated with water, solids, and ash, and it is composed almost entirely of oxygenated hydrocarbons. It has a low heating value, low hydrogen-to-carbon ratio, and high propensity for coking. These factors contribute to its poor quality and to the need for upgrading.

Studies have investigated pyrolysis oil upgrading through numerous pathways. The primary methods are hydrodeoxygenation (HDO) with alumina- or carbon-supported catalysts, catalytic cracking with zeolites, and esterification with alcohol in conjunction with an acid catalyst. Most research has focused on HDO. However, this method involves high hydrogen consumption, which may make it expensive.

Effective upgrading of pyrolysis oil could allow for its use in internal combustion engines. It could also allow for transportation by pipeline. Pipeline transportation is both less expensive and less energy intensive than other methods of shipping, which rely on tanker trucks and ships. The ability to ship pyrolysis oil by pipeline would provide a further advantage over ethanol.

In this study, we have compiled data for 240 raw and upgraded pyrolysis oils from 43 references and have modeled this data. The sources for our database are numbered 1–43. We have compared the physical and chemical properties of pyrolysis oils with the properties of crude oil and with pipeline shipping requirements. We have also examined overlap between pipeline resources and biomass resources. The

analysis of pipelines and biomass is done on a county-by-county basis. This analysis has allowed us to conclude under what conditions the shipment of pyrolysis oil by pipeline is feasible and to comment on upgrading targets necessary to meet the requirements for transportation and of end users.

Because of the complexity of this database and the numerous versions created for unit conversions, data assumptions, and the individual studies presented in this report, we feel that the database is not suitable for stand-alone publication. However, we are available to perform new studies as requested using this database.

1.2 ASSUMPTIONS

In this study, pipeline shipment of pyrolysis oil was evaluated for two areas. First, it was evaluated on a chemical and physical level. In this portion of the study, it was assumed that pyrolysis oil would need to both be very similar to crude oil and emulate current pipeline requirements for crude oil in order to be shipped by pipeline. This area of evaluation also required modeling pyrolysis oil properties and examining upgrading methods that could improve oil to meet this assumption.

The second area on which pipeline shipment was evaluated was the availability of biomass and pipeline resources. Pyrolysis plant size was defined as 400 dry ton per day biomass capacity with a 50 mile collection radius for the biomass, based on discussions with Honeywell's UOP. This size plant should be able to produce approximately 1600 barrels of raw pyrolysis oil per day, or 800 barrels per day petroleum equivalent. This biomass capacity equates to 18.59 dry tons per year per square mile, which is used as our minimum biomass density unit when determining biomass potential of a given county. Counties with this biomass density should be able to support a plant of this size, and counties with greater biomass density could support either a larger plant or a smaller collection radius to decrease transportation costs. Most counties have significantly higher biomass density than our minimum unit.

In this study, pyrolysis plants were also assumed to be feasible only where an appropriate pipeline would be available for transportation of liquid pyrolysis products to an oil refinery, although other means of transportation or use of pyrolysis oils are certainly feasible. Our pipeline data (51) notes the presence of various pipeline types by county, without identifying the actual location within a county. For the purposes of this study, we assumed that to support a pyrolysis plant a county needs either a crude oil collection system (associated with crude oil production) or an intrastate pipeline (associated with crude oil collection, local transportation, or refinery end use). We assumed that interstate pipelines are probably not useful for the injection and transportation of relatively small batches of pyrolysis oil (i.e., 5000 to 10,000 barrels). The presence of liquefied petroleum gas (LPG) or natural gas liquids pipelines are also desirable for transportation of light products but were not used as a decision criteria.

1.3 DATA SOURCES

Pipeline shipment regulation data was taken from a collection of internet references from pipeline operating companies and regulating agencies that provided open information on their websites. These organizations included Sunoco Logistics (48) and Chevron Pipe Line Company (49).

Crude oil property data was obtained for 464 crudes from two online databases. The first was from Chevron's crude oil marketing website (45). This database provided data for 39 crudes on American Petroleum Institute (API) gravity, contaminants, viscosity, pour point, total acid number (TAN), heating value, carbon residues, and several other properties. The other database used was from the Energy Institute HMC-4 Oil Transportation Measurement Committee's website (46) and included data on API gravity, Reid vapor pressure, pour point, viscosity, and other properties for 425 crudes. Both databases provided data on crudes from locations around the world.

Data on pyrolysis oil properties, chemistry, processing, and upgrading was taken from 43 different references (1–43), all published between 1994 and 2011. These references represent a "snapshot" in time and may not reflect currently ongoing research. The compilation of these sources into one data set presented numerous problems. First, different studies measured different properties of oils, which led to an incomplete data set. For example, some papers focused on chemistry and gave elemental compositions and concentrations of specific chemicals, while others focused on physical properties and reported heating values, viscosities, and contaminant levels. Papers that focused on raw pyrolysis oil were often highly descriptive of processing methods, while papers that focused on upgrading often gave little or no information about the raw pyrolysis oil processing conditions. Additionally, different papers frequently measured the same properties with different methods or corrections. It was often possible to correct measurements to reflect the different methods or corrections used, but this process sometimes required assumptions that may have contributed additional variability to the analysis. For example, some studies measured elemental compositions on an as-received basis, while others measured them on a dry basis. In this study, we use the term "as received" to mean without correction to negate the effects of water on measurements. For raw pyrolysis oil, this is synonymous to "as received," but for upgraded pyrolysis oils, "as leaving process" might be a more accurate description. "Wet-basis" is another term that was used in some publications to describe "as-received." Many studies included in our database did not state any basis for measurement, leaving the reader to assume a basis based on the value of the measurement. Similarly, it was not always clear whether a process produced a monophasic or biphasic product, and in biphasic cases it was not always clear which phases were being tested. Although it was possible in many cases to assume the answers to these ambiguities and correct for them, this was not the case for all properties. For example, some papers provided only dynamic viscosity and did not provide a specific gravity, so kinematic viscosity could not be computed. Because of the diverse objectives of, and methods used in, the publications compiled for this study, the final data set was 69% incomplete—that is, only 31% of the cells in the Excel database contain values.

Additionally, there may have been some bias in the data set because different studies contributed different amounts of data, and some authors contributed multiple articles. When significant amounts of data came from one source, similar assumptions were made in experiments, and oils were produced and analyzed under similar conditions. This may have biased the study in the direction of these data points. Although our study attempted to account for this by analyzing the effects of process conditions on outputs, many process factors were not quantified.

Data on the locations of pipelines was obtained by purchase from Hart Energy, who provided a county-by-county listing of pipeline resources (51). Pipeline types included in the study were intrastate, interstate, and gathering crude pipelines for transport of natural gas liquids, liquefied petroleum gas, and crude oil, for a total of nine pipeline types.

Data on biomass resources was taken from the U.S. Billion Ton Update (50), a study of biomass resources in the continental United States. The Billion Ton Update predicts supply curves for different biomass feedstocks on a county scale using several different sets of assumptions. We chose to use the most conservative of these sets of assumptions for our analysis. These assumptions include a gradual move from conventional till to reduced and no-till agriculture, a switch from growing traditional crops to energy crops on cropland when profitable, conversion of cropland used as pasture and pastureland to energy crop cropland when profitable, a 1% annual increase in energy crop yield, and food crop yield increases as predicted by the U.S. Department of Agriculture (USDA). This set of assumptions also includes environmental assumptions concerning the amount of forest or crop residue that can be removed without causing soil erosion and carbon loss. We chose to use a market price for feedstocks of $60 per dry ton because this price is low enough to be realistic and relevant, but high enough that it brings most biomass resources to market.

Although the Billion Ton Update looks at used and unused biomass resources, we chose to include only unused resources in our study. Thus, corn, soybeans, landfill gas, pulping liquors, and most fuelwood, municipal solid wastes, and mill residues are not included in our biomass resource evaluation. Small portions of fuelwood, municipal solid waste, and mill residue are included to the limited extent that they are currently available. Resources that are considered completely unused are agricultural residues, such as corn stover, barley straw, animal fats, waste oils, oat straw, sorghum stubble, and wheat straw, and forest resources, such as trees removed during thinnings and fire treatments, trees removed because of land use change, treetops and small branches from logging operations, and trees grown specifically for biomass as land use changes. Energy crops are considered as beginning in 2014 when seed, seedlings, and cuttings for these crops will likely first be available. The energy crops are grouped in three categories: perennial grasses, which includes switchgrass, miscanthus, and energy cane; woody crops, which include poplar, willow, eucalyptus, and southern pine; and the annual energy crop sorghum. Some of these crops contain higher valued components, such as C5 and C6 sugars or fatty acids which will likely by extracted before pyrolysis and used for other applications. Table 1 summarizes the biomass resources considered in this study.

Data on county size was used in this study to determine biomass density levels. This data was obtained from the U.S. Census Bureau and is based on the 2010 census (46).

Data for pipelines, county sizes, and biomass availability were all taken on a county level. Since these data come from three different sources, there are small discrepancies in the number of counties included. Examples of this include the inclusion of unincorporated townships as separate listings in some databases, and adjustments of counties such as mergers between various census years. We have taken the list of counties from the pipeline resource list as our standard list, deleting or adding entities in the two other databases to match the pipeline list.

Table 1. Resources included in study

Already used biomass resources (not included in study)	Traditional crop resources		Corn (ethanol) Soybeans (bio-diesel)
	Secondary residues		Pulping liquors (process heat and chemicals) Agriculture-based municipal solid waste (landfill gas)
Partially used biomass resources (unused portion included in study)	Forest resources		Fuelwood
	Secondary residues		Mill residues Forest-based municipal solid waste
Unused biomass resources (all included in study)	Energy crops	Perennial grasses	Switchgrass Miscanthus Energy cane
		Woody crops	Poplar Willow Eucalyptus Southern pine
		Annual grasses	Sorghum
	Traditional crop residues		Corn stover Barley straw Animal fats Oat straw Sorghum stubble Wheat straw
	Forest residues		Trees and residue removed during thinnings and fire treatments Trees and residue removed for land use change Treetops and small branches left from logging operations Trees cut for biomass

2. PIPELINE REQUIREMENTS

Information is not available on pyrolysis oil shipment through pipelines, because pyrolysis oil is not shipped by this method currently. However, we have assumed that if pipelines were used for pyrolysis oil shipment, pipeline companies would likely require pyrolysis oils to meet the same standards as for crude oils. These requirements regulate the vapor pressure, specific gravity, contaminants, and viscosity of crudes submitted to pipelines. Vapor pressure is regulated for pollution prevention and is usually capped between 8 and 11 psig at 100°F depending on season, local climate, and density of crude. Federal, state, and local laws regulate vapor pressure in pipelines, and limits are translated into standards provided by pipeline companies. Viscosity and specific gravity are important factors for pipeline shipment because more viscous and heavier oils require more energy to ship and may reduce pipeline capacity. Most pipeline companies will not ship crudes more viscous than 75 cSt at 100°F, and many charge a viscosity tariff of up to 118% on oils starting with viscosities above 10 cSt at 100°F. The price and starting viscosity for this tariff varies from one pipeline to another. Similarly, most pipeline companies will only ship crude with a specific gravity between 0.563 and 0.934, although a few will accept specific gravities up to 0.979, and some have price scales that are dependent on specific gravity and favor lighter crudes. The lower end cap of 0.563 does not seem relevant to either crude or pyrolysis oil, as neither ever approaches this density. Contamination requirements tend to group “foreign sediment and water” and cap them between 1 and 2%. Some companies also specifically prohibit iron, lead, and organic chlorides above certain levels.

Pyrolysis oil has many problems, including corrosiveness and high concentrations of oxygenated hydrocarbons, that could be detrimental to pipeline infrastructure and are not common problems with crude oil. Because these problems have not been associated with crude oil, pipeline companies have not specifically regulated properties like pH, TAN, and oxygen content. However, we have assumed that they would begin to regulate these properties if pyrolysis oil were shipped through pipelines, and that they would require pyrolysis oil to be very similar to crude oil with regard to these properties. Language in pipeline requirements prohibits the “presence of any excessive metals or chemicals including but not limited to chlorinated and oxygenated hydrocarbon” and preserves the right to inject corrosion inhibitors (47). This suggests that pipeline companies would take action against corrosion and other forms of contamination if these problems became an issue.

3. CRUDE PROPERTIES

The average values for various properties of the crude oils examined in this study are presented in Table 2. As expected, average values for specific gravity and Reid vapor pressure fall well within the pipeline shipment limits stated previously. For both of these properties, however, crude oils that do not meet shipment criteria were included in the database. Crude specific gravities were as high as 1.02, and Reid vapor pressures were as high as 11.9 psig. These heavy crudes and high-vapor-pressure condensates require special handling and are shipped in specially designed pipelines. This study only considers typical US pipelines and typical US pipeline requirements.

Table 2. Crude oil properties

Property	Mean	Median	Max	Min
Gravity, °API	35.38	35.30	74.5	7.9
Specific gravity	0.85	0.85	1.02	0.69
Sulfur, wt %	0.48	0.2	3.97	0.01
Mercaptan sulfur, ppm	98.65	3	592	1
Nitrogen, ppm	1298.51	1018.5	4420	0.232
Hydrogen, wt %	13.16	13.3	15.3	11.4
Viscosity @ 40°C (104°F), cSt	59.24	5.19	3080	0.5
Viscosity @ 50°C (122°F), cSt	17.84	3.91	236.6	0.5
Viscosity @ 100°C (212°F), cSt	4.46	1.96	25.9	0.42
Viscosity @ 135°C (275°F), cSt	2.24	1.24	11.5	0.364
Pour point, °C	-15	-15	48	-63
Pour point, °F	18	25	100	-65
Total acid number (TAN), mg KOH/g	0.34	0.1	2.41	0
Characterization factor (K factor)	12.0	12	12.7	11.59
Molecular weight	249	223	490	111
Gross heating value, MM BTU/bbl	5.83	5.79	6.24	5.25
Gross heating value, kcal/kg	10908	10960	11340	10350
Gross heating value, MJ/kg	45.65	45.85	47.5	43.3
Heptane asphaltenes, wt %	0.9	0.2	6.4	0
Micro carbon residue, wt %	2.9	1.7	11.3	0
Ramsbottom carbon, wt %	2.8	1.6	10.5	0
Vanadium, ppm	11.2	1	152	0
Nickel, ppm	8.0	3	43.8	0
Iron, ppm	3.3	2	13	0
Reid vapor pressure, psi	4.3	4.3	11.9	0

The average viscosity of crude oil at 40°C (104°F) was 59.24 cSt, which is very near the upper limit of the pipeline shipment range and well above the limit for shipment without tariffs. The median viscosity at 40°C, however, was only 5.19 cSt, more than 10 times less than the mean. Thus, most crudes still fall in in the no-tariff viscosity region. Specifically, 69.9% of crudes in our study had viscosities less than 10 cSt at 40°C, and 87.18% had viscosities less than 75 cSt at 40°C. The high mean value for viscosity at 40°C

was driven by the extremely high viscosities that very few oils presented. The maximum viscosity seen at 40°C was 3080 cSt, but only 6 of the 464 crudes had viscosities greater than 500 cSt at 40°C. Viscosity measurements taken at other temperatures showed similar distribution trends. These high-viscosity crudes are often heated above 40°C to reduce shipped viscosity and allow for handling and shipment.

Total acid number measurements are distributed similarly to viscosity. That is, most oils had very low TAN, but a select few had much higher TANs than others. This effect was not as extreme for TAN as it was for viscosity; the mean is only 3 times greater than that median. Also, even the most acidic crude in our database had a TAN of only 2.41 mg KOH/g oil.

4. PYROLYSIS OIL PROPERTIES AND CHEMISTRY

4.1 WATER

Water content in raw and treated pyrolysis oils ranged from 0% to 70%. It was reduced by upgrading, with the mean water content dropping from 22.52% to 7.92% with upgrading. Neither raw nor upgraded pyrolysis oil consistently had less than 2% water as required by pipelines for shipment. Only 6.3% of raw oils and 32.4% of upgraded oils had less than 2% water. A frequency diagram illustrating the reduction in water from upgrading is provided in Fig. 2. This frequency diagram, and others throughout this report, places bin numbers directly below data bars. The height of the bar indicates the percentage of data that was less than or equal to this number but did not fall in a lower bin. For example, the first bar in Fig. 2 represents the percentage of oils with 0% water, and the second bar represents the percentage of oils with more than 0% but less than or equal to 5% water. In Fig. 2, bins are of equal size; however, other frequency diagrams in this report use bins of varying size to give a more appropriate representation of data. Trend lines on frequency diagrams in this report show a 2-point moving average, unless otherwise noted.

Several raw pyrolysis oil samples were reported to contain no moisture. These results were achieved by fractioning pyrolysis oil into aqueous and oil phases and only reporting measurements for the oil phase. Although this method does appear to be effective in reducing water content, and possibly in reducing acidity as well, all of the carbon in the aqueous phase is lost when fractionation is used. This can lead to very low yields. Another method that has been used to achieve low water content in raw pyrolysis oils is to correct the values to a moisture-free basis and then report all values, including moisture, on this basis.

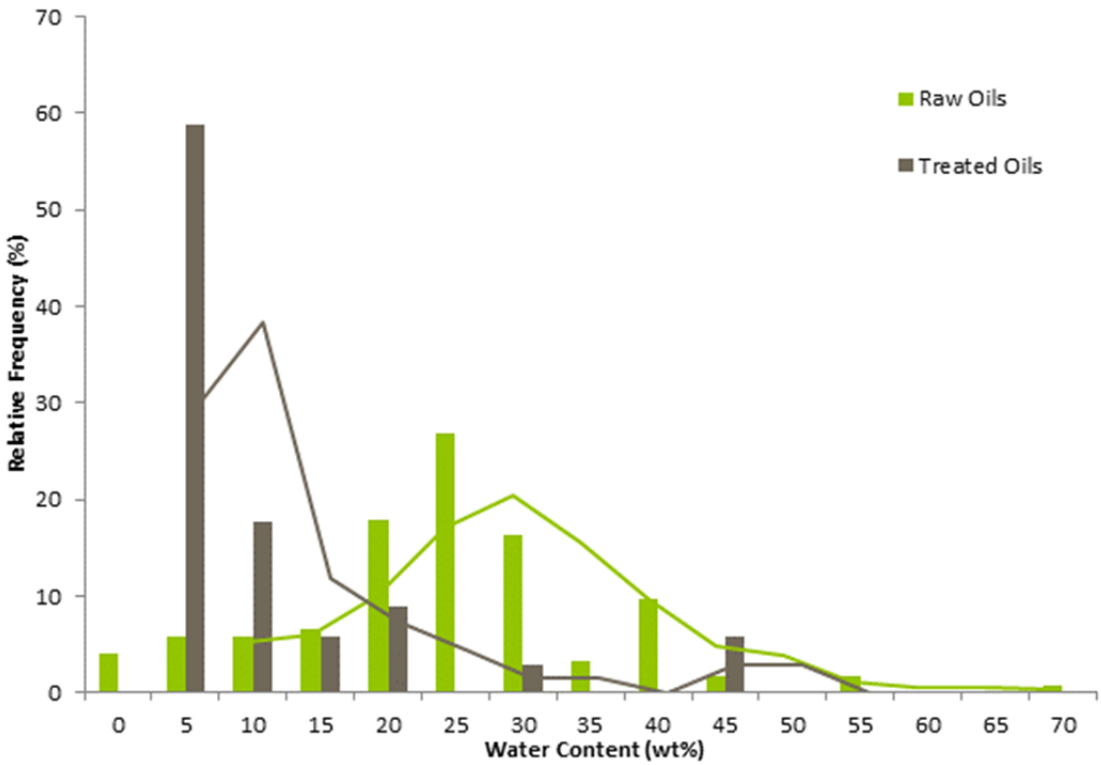

Fig. 2. Water content in raw and upgraded pyrolysis oil, with trend lines showing a 2-point moving average. See related text for a description of *x*-axis bins for graphs of this type.

4.2 ELEMENTAL COMPOSITION

Minimum, maximum, and average values for oxygen, carbon, and hydrogen content in both raw and treated pyrolysis oils are presented in Table 3. Values in the table are mass percentages on an as-received basis. Although not all elemental analysis data was provided on an as-received basis, it was usually possible to convert between a dry and as-received basis using ASTM D3180. However, the data needed for this conversion was not always available, so there are some discrepancies between the elemental data on the two bases. Further, it was not always possible to discern on which basis the data had been collected, leading to possible errors in the data sets.

Table 3. Elemental analysis of raw and treated pyrolysis oils, on a mass percentage as-received basis
(Note that the individual numbers are not from the same oils.)

	Raw Pyrolysis Oil			Treated Pyrolysis Oils		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**
Oxygen	44.58	68.52	10.52	21.51	50	0.34
Carbon	47.84	79.90	22.44	68.29	87.66	41.5
Hydrogen	7.57	11.78	3.37	9.06	12.9	6.7

Oxygen content is reduced by upgrading processes, which was expected because oxygen is usually the primary target of upgrading. Oxygen content on an as-received basis represents the two components of pyrolysis oil that cause most of the differences between it and crude oil—water and oxygenated hydrocarbons—making it a useful benchmark measurement. We have translated the 2% water limit and prohibition on excessive oxygenated hydrocarbons given in pipeline specifications into a 2% as-received oxygen limit. The mean as-received oxygen content in treated pyrolysis oils is more than ten times this limit; however, one study in our database produced pyrolysis oils below this limit (12). This is significant because it shows that upgrading to our assumed pipeline quality is possible.

The contents of both carbon and hydrogen increased in treated pyrolysis oil. The increases in carbon and hydrogen are largely due to the reduction in total mass as oxygen is removed. However, some of the hydrogen content increase seen in upgraded pyrolysis oils is the result of hydrogen addition during hydrodeoxygenation treatment processes, which improve the H:C ratio. The difference in oxygen and carbon contents between raw and treated pyrolysis oils can be seen in Fig. 3.

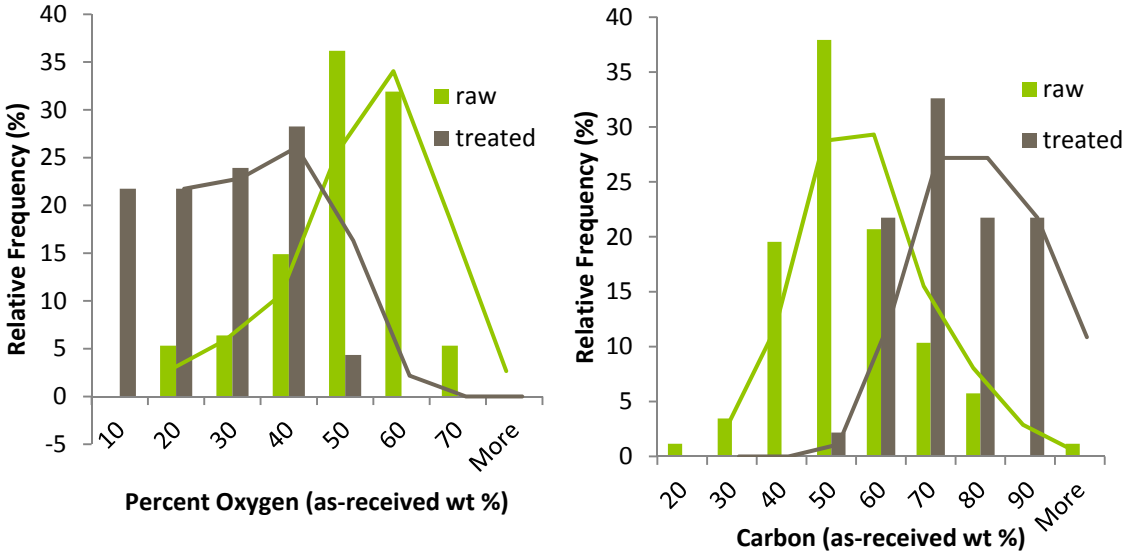

Fig. 3. Relative frequencies of oxygen and carbon contents in raw and treated pyrolysis oils (lines show 2-point moving average).

The only elemental analysis of crude oil that was available was for hydrogen. Hydrogen contents in raw and treated pyrolysis oil and crude oil are compared in Fig. 4. Although hydrogen content in treated pyrolysis oils is significantly higher than hydrogen content in raw oils, both are still significantly lower than hydrogen content in crude oils. Some of the difference in hydrogen content between pyrolysis oils and crude oils can be accounted for by the presence of oxygen in pyrolysis oils, since a significant oxygen content leaves less room for hydrogen. Another explanation for higher hydrogen content is a higher molar H:C ratio. H:C ratio is an important measure of fuel quality, so the lower hydrogen contents in pyrolysis oils could signal that pyrolysis oil is a lower quality fuel than crude and will require additional upgrading at a refinery.

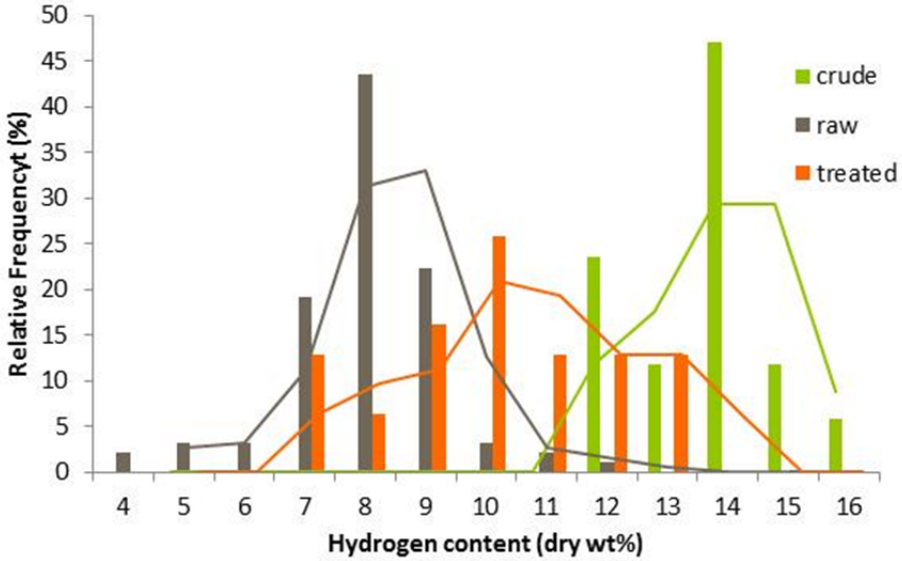

Fig. 4. Hydrogen content in raw and treated pyrolysis oils and crude oil (lines show 2-point moving average).

To further investigate the molar H:C ratio in pyrolysis oil, this value was calculated for crude oil and pyrolysis oil samples in the database. For pyrolysis oil, it was calculated on both an as-received and dry basis. The ratio calculated on a dry basis was deemed the more appropriate measure for comparison to crude, as hydrogen in the water does not contribute to heating value. To calculate H:C ratio for crude oil, we assumed that crude oil was composed entirely of hydrogen and carbon. The only elemental analysis available for crude was hydrogen content, so this assumption was necessary to calculate carbon content. The frequency graph shown in Fig. 5 shows that crude oil has a higher H:C ratio than raw or treated pyrolysis oil, and that treated pyrolysis oil has a higher H:C ratio than raw pyrolysis oil. As expected, the distribution of H:C ratios is very similar to that of hydrogen content.

H:C ratio calculations were affected by the ambiguity about the basis of the elemental analysis. It is assumed that incorrect assumptions of dry basis led to the calculation of dry H:C ratios greater than 2. This is because the formula for alkanes, which have the highest H:C ratio among the hydrocarbons, is C_2H_{n+2}, and pyrolysis is composed of large hydrocarbons, most of which are not alkanes and thus have H:C ratios lower than 2, so it is unlikely that pyrolysis oil samples actually have a H:C ratio greater than 2.

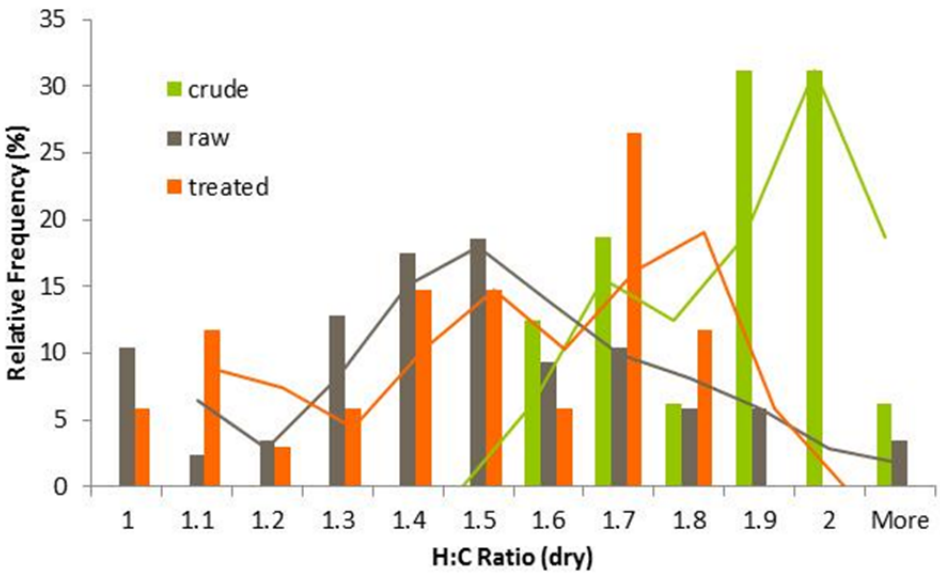

Fig. 5. Molar H:C ratio calculated on a dry basis in crude oils, raw pyrolysis oils, and treated pyrolysis oils. Lines show 2-point moving average.

H:C ratio on an as-received basis was significantly higher than H:C ratio on a dry basis. This was expected because water is 11% hydrogen and 0% carbon, so it increases hydrogen content in pyrolysis oils with less than 11% hydrogen, which is most pyrolysis oils, while lowering carbon content by dilution in all pyrolysis oils. Thus, H:C ratios of greater than 2 are possible and occur frequently in raw pyrolysis oil when the ratio is calculated on an as-received basis. As can be seen in Fig. 6, the as-received H:C ratio was lowered by upgrading, which was also expected because upgrading removes water from oils.

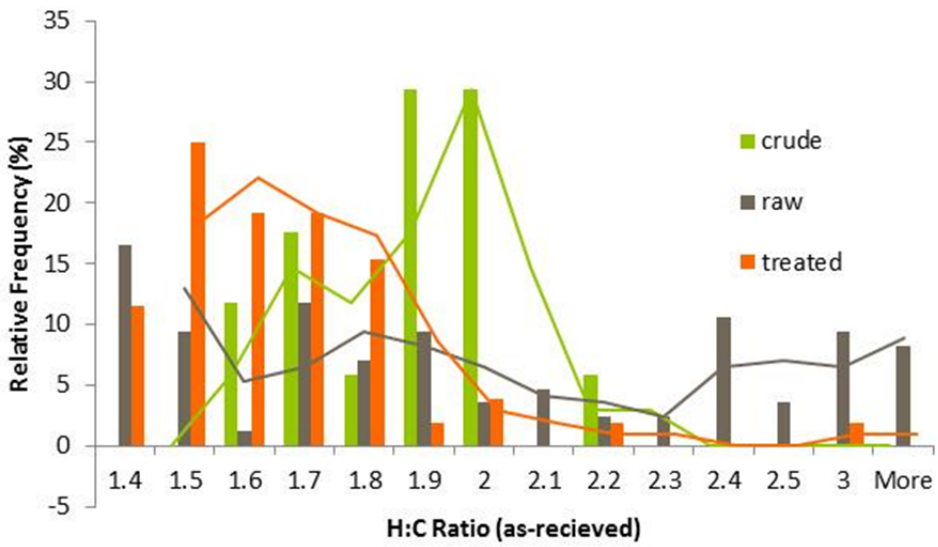

Fig. 6. Molar H:C ratio calculated on an as-received basis in crude oils, raw pyrolysis oils, and treated pyrolysis oils. Lines show 2-point moving averages.

4.3 HEATING VALUE

Data on heating value was provided in four forms: higher heating value (HHV) on a dry basis, HHV on an as-received basis, lower heating value (LHV) on a dry basis, and LHV on an as-received basis. Conversion between HHVs and LHVs was completed as described in ASTM D5865. This standard provides equations that account for the energy change from the vaporization of water produced from hydrogen in the sample, the energy change from the vaporization of water received in the sample, and the energy change associated with the volume change in the calorimeter as water condenses or is vaporized. ASTM D3180 also provided needed equations for moving between elemental analyses or heating values on a dry basis to those on an as-received basis. However, there was not always enough information provided on a given oil to complete these conversions, so data on one basis does not correlate perfectly with data on other bases. In general, HHV on an as-received basis was considered the most significant measurement because pyrolysis oil will be used or shipped with water present and HHV is more easily measurable than LHV in a bomb calorimeter. In some cases when subsets of data were being examined, significantly more data was available for LHV or on a dry basis, so these bases were used.

As-received HHV in raw and treated pyrolysis oils ranged from 11.1 MJ/kg to 44.0 MJ/kg, while as-received HHV in crude oils ranged from 43.3 MJ/kg to 47.5 MJ/kg. Heating value improves when pyrolysis oils are upgraded, with the mean HHV increasing from 20.612 MJ/kg to 27.52 MJ/kg, but is still far lower than HHV in crude oil. Improvement from upgrading is compared to heating value of crude oils in Fig. 7. The increase in heating value after upgrading is still present when heating value is calculated on a dry basis. Mean dry HHV increases from 25.32 MJ/kg to 32.59 MJ/kg with upgrading, which shows that heating value increases as a result of removing both water and dry oxygen.

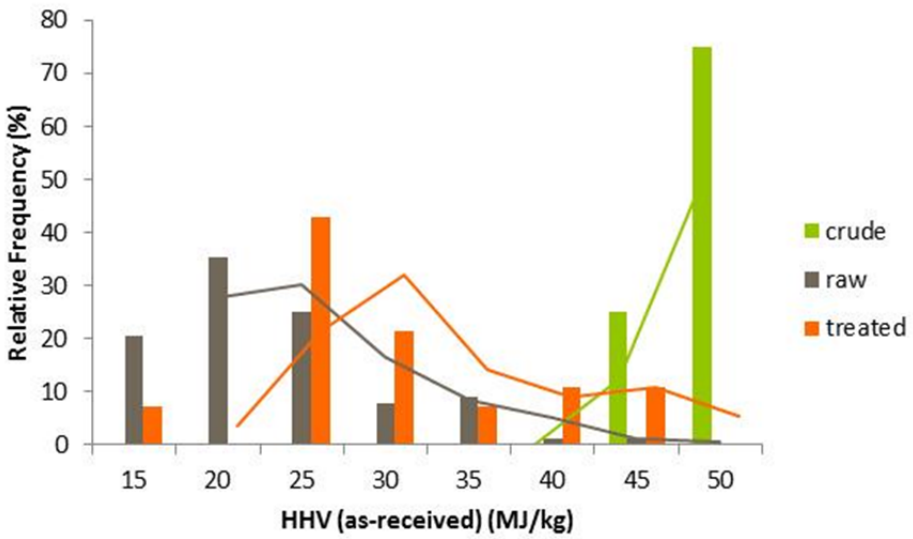

Fig. 7. Relative frequencies of higher heating values (calculated on an as-received basis) with trend lines showing 2-point moving averages.

Negative correlations have been seen between heating values of pyrolysis oils and both oxygen and moisture contents. This was expected because water cannot be burned, so it dilutes the hydrocarbons without contributing directly to the heat of combustion. Additionally, oxygenated hydrocarbons release less energy when burned than non-oxygenated hydrocarbons. This relationship holds true for treated and untreated oils, whose trend lines appear to be contiguous although they cover different ranges. As can be seen in Fig. 8, the treated oils fall on about the same trend line as raw oils when plotting HHV against oxygen or moisture content. However, treated oils are distributed at lower moisture or oxygen contents and higher heating values, while raw oils are concentrated at higher moisture or oxygen contents and lower heating values.

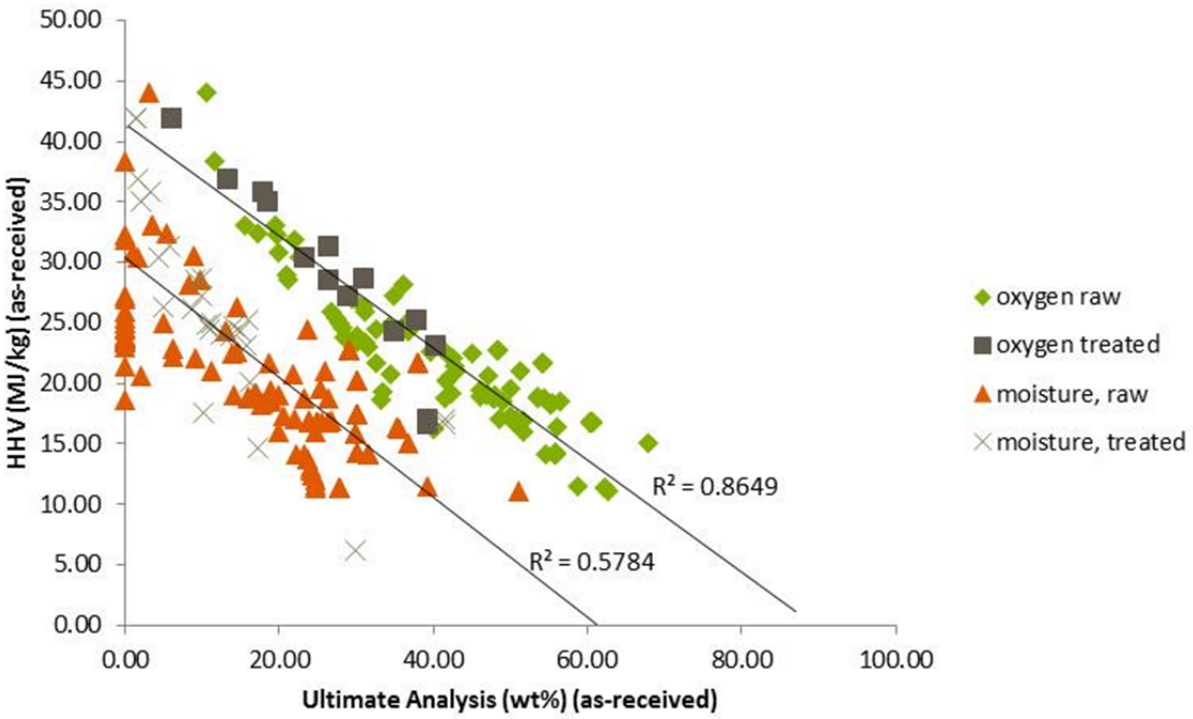

Fig. 8. Relationship between higher heating values and oxygen and moisture contents of both raw and treated oils.

4.4 SPECIFIC GRAVITY

The specific gravity of pyrolysis oils ranges from 0.81 to 1.29. Specific gravity appears to be significantly and consistently improved through catalytic upgrading processes of all types. As can be seen in Fig. 9, raw and treated oils clearly form separate populations of oils with respect to specific gravity. Treatment shifted the range of specific gravities of pyrolysis oils from 0.91 to 1.29 for raw oils and from 0.81 to 1.00 for treated oils, and shifted the mean specific gravity from 1.18 to 0.89. Figure 9 also illustrates the significant overlap between treated and crude oils and shows that 73.9% of the treated pyrolysis oils in our study fall into the pipeline shipment range of less than 0.934.

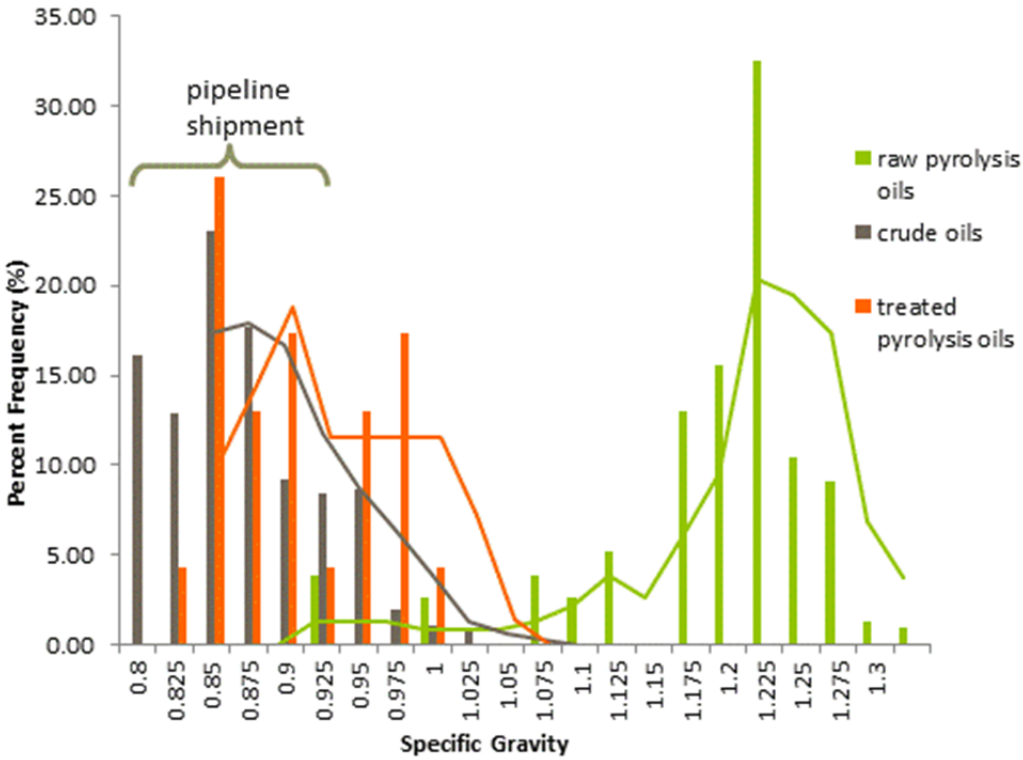

Fig. 9. Specific gravities of raw and treated oils (lines show 3-data point moving averages).

4.5 VISCOSITY

The kinematic viscosity of both treated and untreated oils at 40°C varied greatly between samples. For some pyrolysis oils, this measurement was provided, whereas for others it was calculated from dynamic viscosity and specific gravity or calculated based on measurements at a temperature other than 40°C. To estimate viscosity at 40°C based on viscosity at other temperatures, we derived an empirical equation to describe the behavior of pyrolysis viscosity with respect to temperature. This equation was derived by looking at publications in which viscosity of one sample was given at multiple temperatures. We used Microsoft Excel to plot these sets of temperature and viscosity data as different series on one graph. Excel's regression capabilities allowed us to fit different types of equations to each data set. To develop our predictive equation, all the data sets needed to be represented well by a single type of equation (i.e. linear, exponential, etc.), and only one coefficient in this equation could differ significantly between data sets. The data was fit to linear, polynomial, power, and exponential equations, and a power equation appeared to fit best. The data sets used for this analysis can be seen in Fig. 10, with trend lines representing power regressions. When comparing the data with power equation representations, the average coefficient of determination for each oil was 0.9639. Further, one of the coefficients had a standard deviation of only 22.17% of its value, so it varied comparatively little between data sets. The average value of the coefficient that varied less was calculated, giving the equation $v = aT^{-2.23}$. This equation was then used to estimate kinematic viscosity at 40°C for oils where viscosity was provided at a single, different temperature. For oils with viscosity measurements provided at multiple temperatures not including 40°C, the regression equations of power form, determined by Microsoft Excel, were used for this estimation.

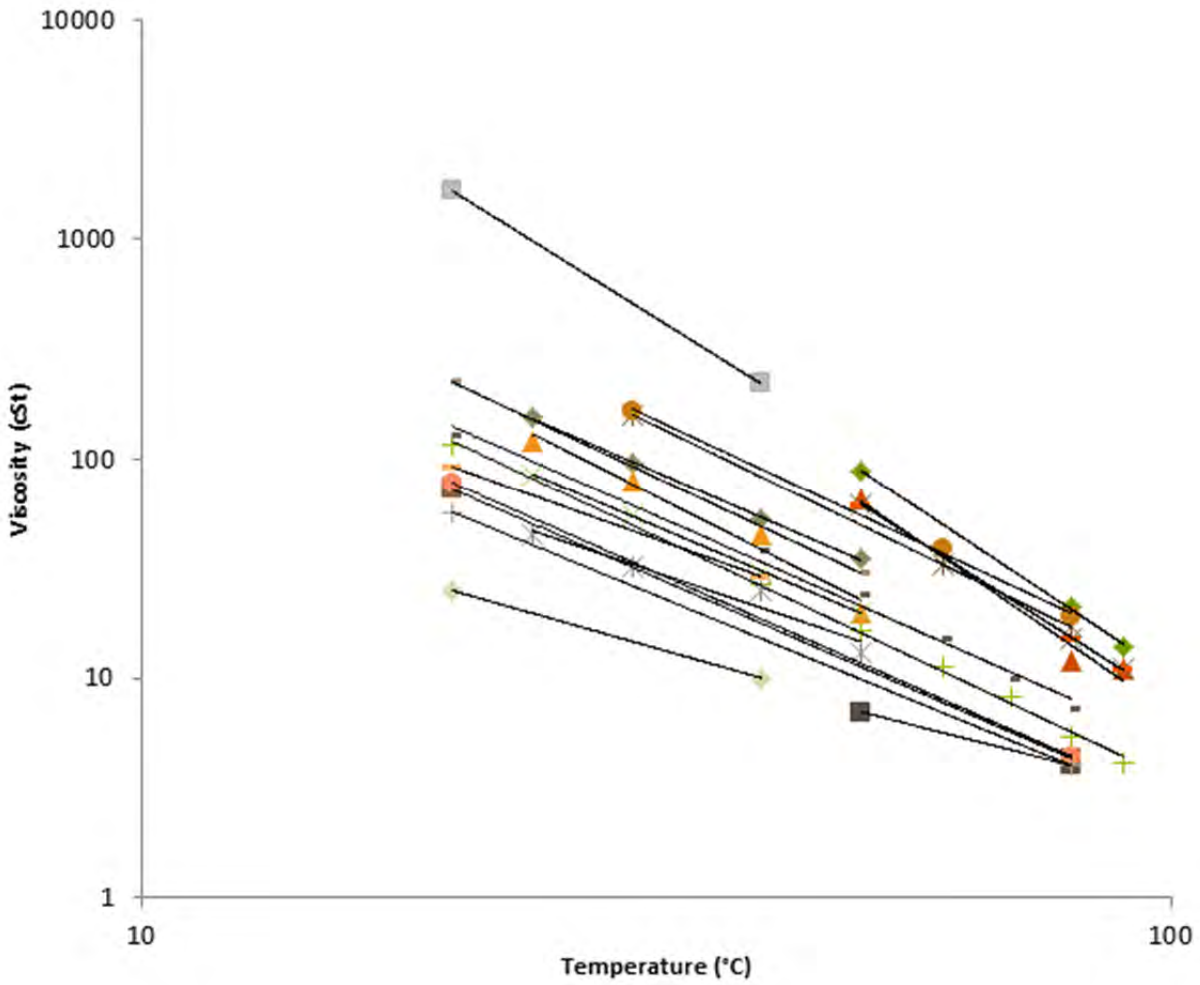

Fig. 10. Viscosities of pyrolysis oils at multiple temperatures fit to power equations. Symbols indicate all samples of pyrolysis oil for which viscosities were available at multiple temperatures.

The kinematic viscosity at 40°C correlated only with average molecular weight, as determined by light scattering. Unfortunately, the average molecular weight was provided for only four samples, so this correlation may not apply to all oils. The positive correlation between average molecular weight and viscosity was expected because high molecular weight indicates the presence of bulky polymers. The correlation between viscosity and molecular weight is also seen in the crude oil data. For both the crude oil and pyrolysis oil data sets, the viscosity–molecular weight correlation seems best modeled with an exponential equation. The trend lines for the two data sets neither have the same shape nor are close together, suggesting that the relationship between viscosity and molecular weight is different for pyrolysis and crude oils. These relationships can be seen in Fig. 11.

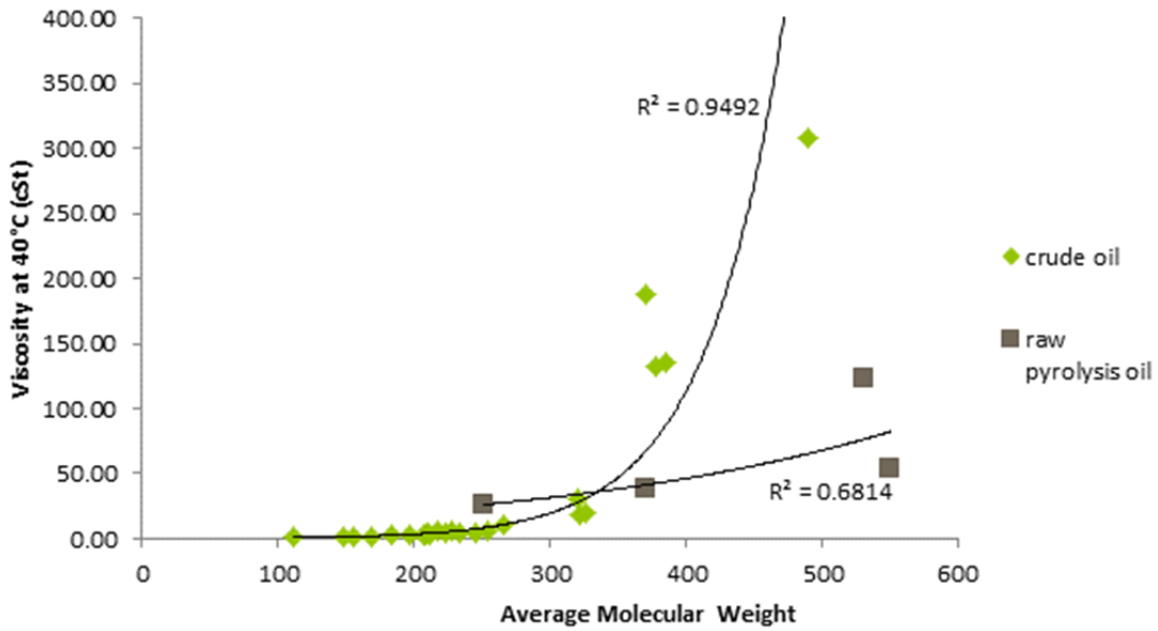

Fig. 11. Correlation between viscosity and average molecular weight in crude oils and raw pyrolysis oils.

Although individual studies in our database indicate a correlation between water and viscosity, the overall relationship that we found had a correlation coefficient of only 0.43, which we do not consider significant. Figure 12 shows this relationship and the large amount of spread in the data. Within a single study with very similar sample processing conditions, water may correlate with viscosity; however, when looking at samples from multiple studies processed in very different ways, this relationship shows much more variability. Generally, viscosity is expected to increase as water is removed and then decrease at lower water contents, which indicates overall chemistry improvements for pyrolysis oil.

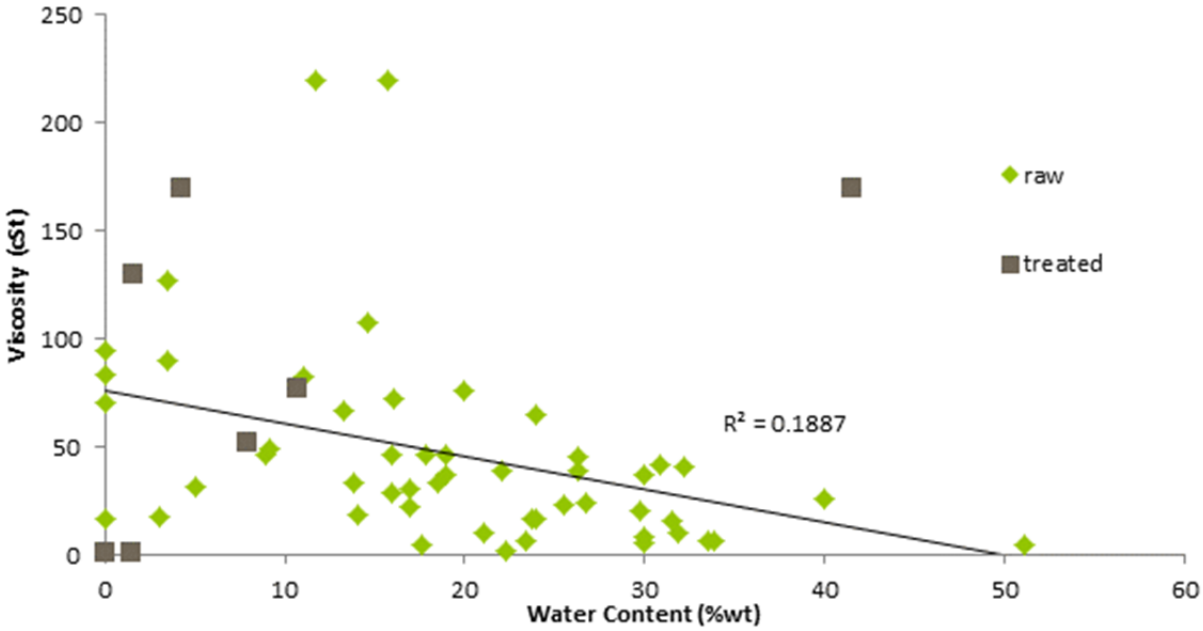

Fig. 12. Relationship between water and viscosity.

The average viscosity of a raw pyrolysis oil sample is 64.5 cSt at 40°C. While this is low enough to ship in most pipelines, an oil of this viscosity would likely be subject to tariffs. Further, because the viscosities of oils varied greatly, some as high as 1666 cSt at 40°C, they could not be shipped by pipeline as is. Pipeline shipment requirements, crude viscosities, raw pyrolysis viscosities, and upgraded pyrolysis oil viscosities are compared in Fig. 13.

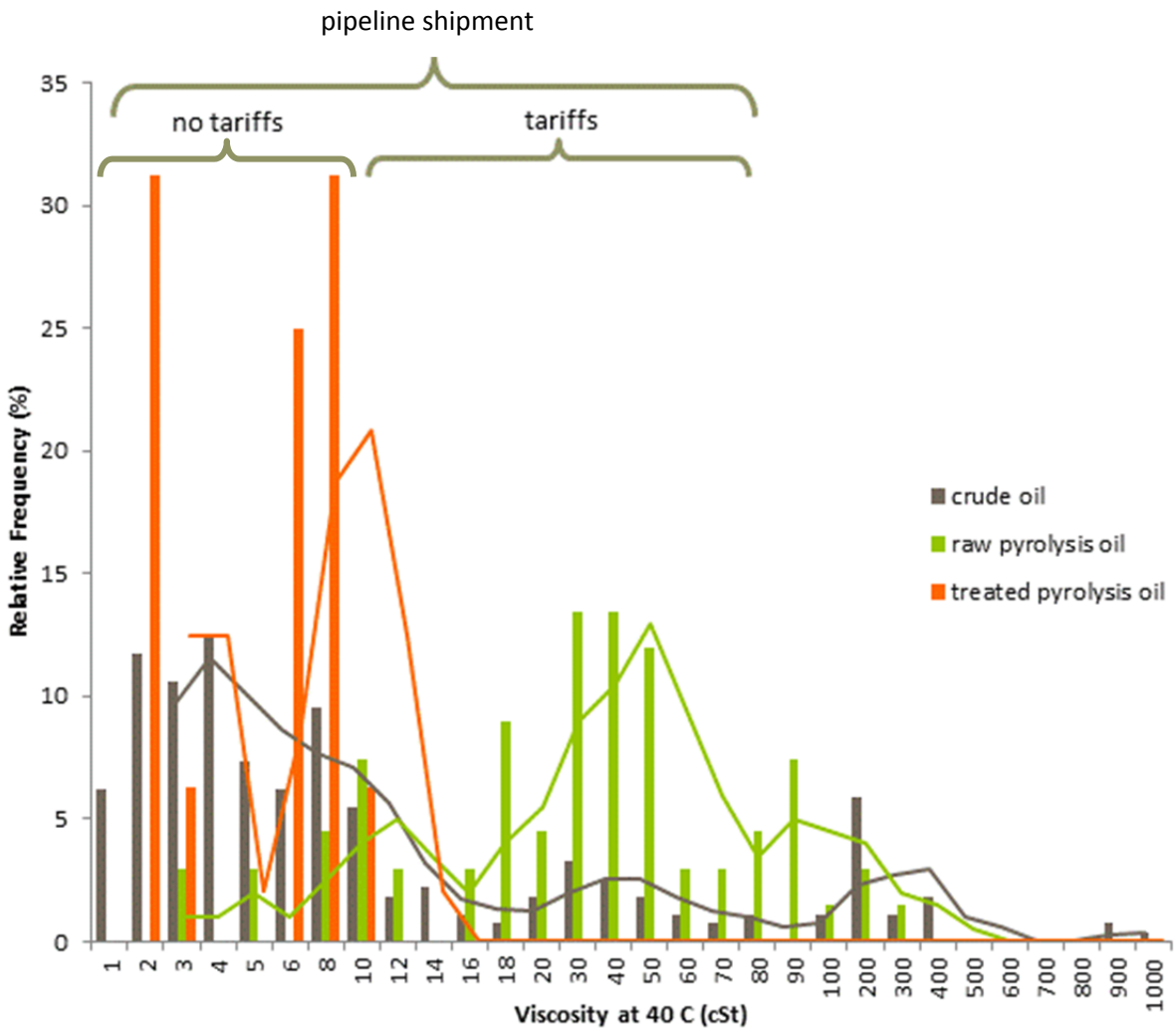

Fig. 13. Relative frequencies of viscosities of crude, raw pyrolysis, and treated pyrolysis oils compared with pipeline shipment requirements.

In-house viscosity testing was performed for one sample, provided by UOP. The viscosity was measured in a rotational viscometer, using the cup-and-bob geometry. The viscosity was measured at 20, 40, 60, 80, and 100°C at shear stresses ranging from 1 to 500 dyne/cm^2. The pyrolysis oil appeared to be Newtonian at 20°C, shear thinning from 40 to 60°C, and shear thickening above 80°C. Further measurements were not performed because sufficient data was available from the literature search. We also note that we were unable to measure viscosity with an automated falling ball viscometer because the opacity of the samples precluded the use of a method that uses light to sense ball motion.

Upgrading appears to significantly reduce viscosity. The average viscosity of upgraded oils was only 5.8 cSt at 40°C, which is low enough to ship with no tariff. All of the treated oils for which viscosity data was available had viscosities low enough to be shipped, and 88.9% could likely be shipped without a tariff.

4.6 ACIDITY

Acidity was measured in two ways in the studies included in our database: pH and TAN. As can be seen in Fig. 14, pH and TAN do not have a linear relationship. Thus, it is difficult to compare changes in pH that occur in highly acidic oil to those that occur in more neutral oils. Additionally, pH testing measures ions in aqueous solution, and pyrolysis oil has at least one phase that is not an aqueous solution. Figure 15 shows that upgraded pyrolysis oils may split into two populations, one having pH significantly higher than raw oils and the other having about the same pH as raw oils. However, because these two populations each represent data from different single authors, it is difficult to draw more general conclusions about pH which are representative of all upgraded pyrolysis oils.

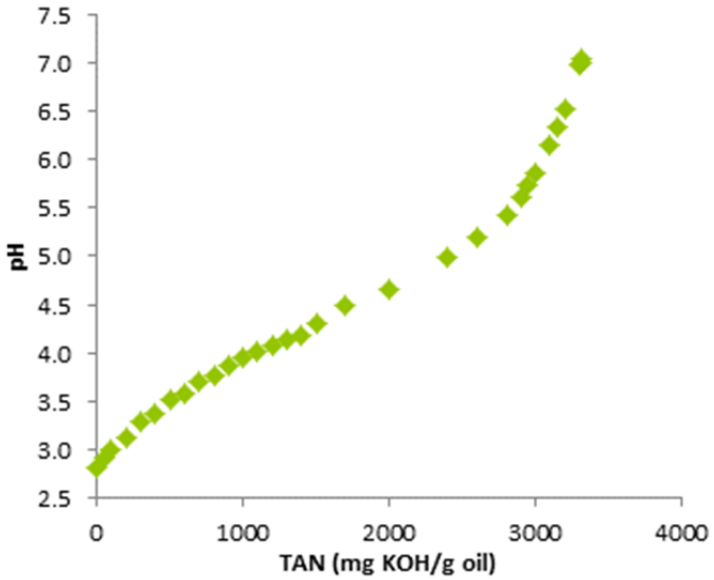

Fig. 14. Titration curve from titration of USDA treated pyrolysis oil sample using a water-extraction approach (Raynella Connaster, ORNL).

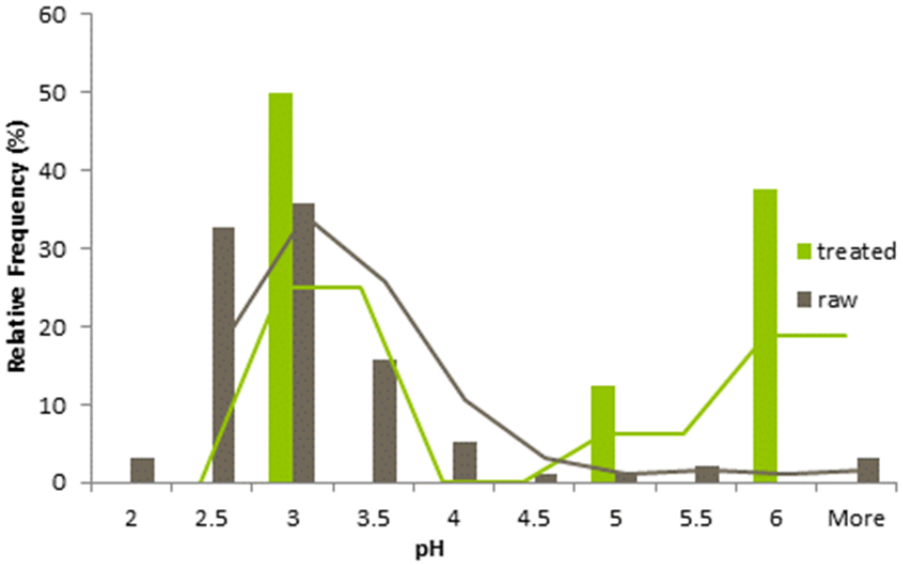

Fig. 15. Relative frequencies of pH in raw and treated pyrolysis oils (trend line is 2-point moving average).

TAN analysis of oils is somewhat less ambiguous relative to acidity. TAN in crude oil is generally two orders of magnitude less than TAN in raw pyrolysis oil. As can be seen in Fig. 16, treated pyrolysis oils fall into two populations. One population has a TAN about half that of raw pyrolysis oils. The other population has a TAN only slightly higher than that of crude oil. This second population contains only pyrolysis oils from one study (12) where pyrolysis oil was hydrotreated in a two-step process.

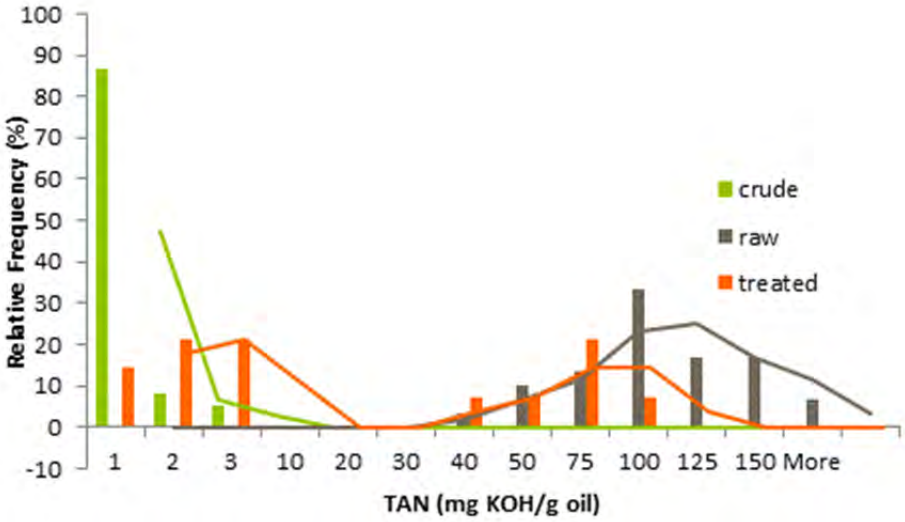

Fig. 16. Relative frequencies of TAN in crude oils and raw and treated pyrolysis oils (trend line is 2-point moving average) (note nonlinear scale).

In addition to correlating with upgrading, TAN appears to correlate with water content. This correlation can be seen in Fig. 17. This correlation may partially result because water and TAN are both targets of upgrading processes and are both reduced in upgraded oils. However, this may also have a direct causal relationship. Compounds that contribute to TAN include carboxylic acids, phenols, esters, and other

acidic compounds. Many of these compounds are water soluble, so when pyrolysis oil is split into aqueous and oil fractions, acidic compounds and water may be removed at the same time.

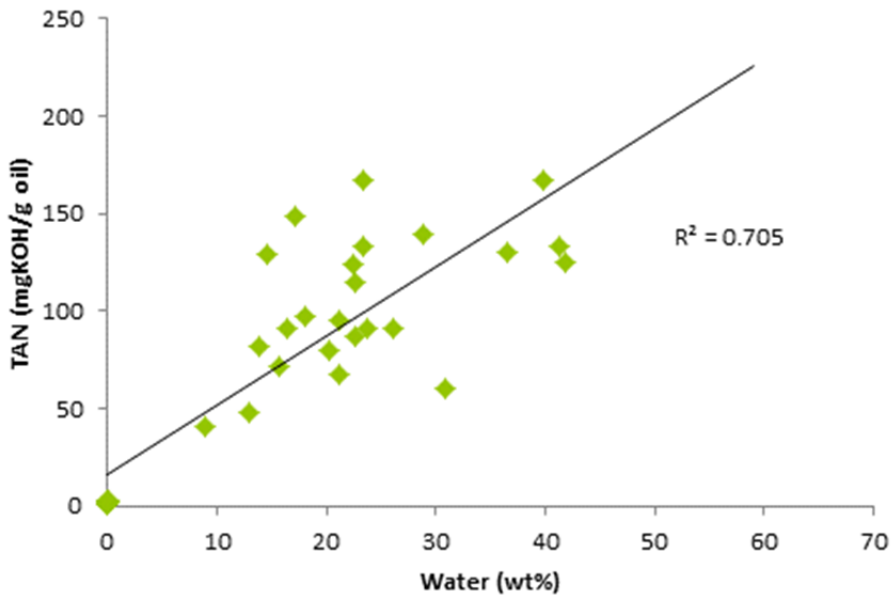

Fig. 17. TAN and water content in raw and treated pyrolysis oils.

4.7 CONTAMINATION

Pyrolysis oils are typically contaminated with solids, ash, sulfur, and nitrogen. The ash content ranges from 0 to 1.5 wt %; the solids content, from 0.007 to 1.02 wt %; the dry sulfur content, from 0 to 0.39 wt %; and the dry nitrogen content, from 0 to 7.57 wt %. There is ambiguity in the measurements of solids, sulfur, and nitrogen. Some groups define solids as insoluble in ethanol, while others use solubility in methanol as criteria. Also, in many articles it was unclear whether the sulfur and nitrogen contents reported were on an as-received basis, a dry basis, or a dry ash-free basis.

Most pipeline specifications group water and solids in one category, with a limit between 1 and 2%. Because water makes up such a high portion of both raw and upgraded pyrolysis oils, solids and ash are often considered an insignificant issue in comparison. However, reduction of solids and ash would allow more water to be left in pyrolysis oil, and such a reduction might be required for the shipment of some oils in some pipelines. To our knowledge, there is currently no data available on the effects of upgrading on either solid or ash content, but both would be expected to improve.

Pyrolysis oil appears to be significantly less contaminated with sulfur than are crude oils. The range of sulfur in crude oil stretched from 0.01 to 3.97 wt %, so the crudes with the most sulfur contained ten times more sulfur than the raw pyrolysis oils with the most sulfur. Further, the average sulfur content of crudes was 0.48 wt %, while the average for raw pyrolysis oils was only 0.07%. Although reduction of sulfur content in pyrolysis oils does not appear necessary, it may be reduced when pyrolysis oil is upgraded for other reasons. The average dry sulfur content dropped to 0.04% after upgrading, and the p-value for this difference was 0.18.

Nitrogen content in both raw and upgraded pyrolysis oils was higher than in crude oils. The average dry nitrogen content in pyrolysis oils was 0.86% for raw oils and 0.62% for upgraded oils, while the average nitrogen content in crude was only 0.13%. Nitrogen content also had a much wider range in pyrolysis oils

than in crude oils. This is likely an effect of feedstock. Feedstocks with high nitrogen produce pyrolysis oils with high nitrogen. For example, one oil in our database had significantly higher nitrogen content than any of the others. This oil was produced from chicken litter, which is a mix of chicken bedding and droppings. Because it includes chicken waste, it has a higher nitrogen content than other feedstocks. This was the only oil in our data set that was derived from animal waste, but it could be expected that any animal-waste-derived oil may have a high nitrogen content. High nitrogen content is undesirable in transportation fuels because it can affect stability and color and can convert to nitrogen oxides during combustion. Additionally, removal of nitrogen increases hydrogen consumption during upgrading.

There are strong correlations between sulfur, ash, and solid content in pyrolysis oil. These relationships can be seen in Fig. 18. These relationships are probably caused by an outside factor, rather than being causal relationships. Also, overlap between some of these measurements may cause this correlation. Ash often has a relatively high sulfur content, so when sulfur is not measured on an ash-free basis, ash with high sulfur content could explain this correlation. Similarly, many solids in pyrolysis oil, like those containing trace minerals, become ash when pyrolysis oil is burned. So, a high noncombustible solid content would mean both high solid and ash contents, leading to a positive correlation between solids and ash. Alternatively, these correlations may be a sign that sulfur, ash, and solid contaminants are removed together during pyrolysis or upgrading processes.

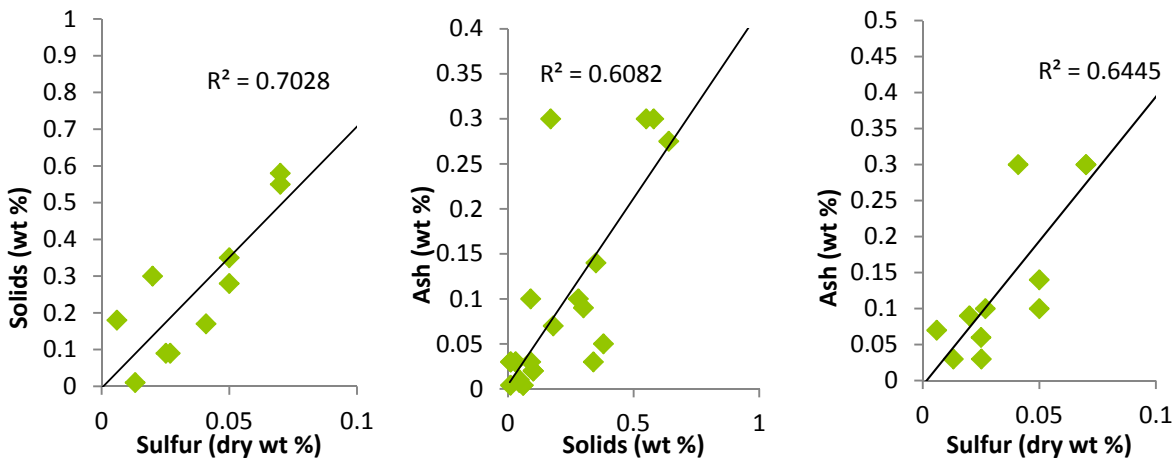

Fig. 18. Correlations between sulfur, ash, and solids in pyrolysis oils.

4.8 POUR POINT AND FLASH POINT

The pour point of pyrolysis oil is important for transportation or use at low temperatures. The pour point of raw pyrolysis oil ranged from -42°C to 25°C. This range was very similar to the range of pour points for crude oil, which varied from -63°C to 48°C. Pour point was not measured on any upgraded pyrolysis oils. Flash point of pyrolysis oil is important for safety concerns. Flash point in raw pyrolysis oil ranged from 42°C to 110°C. Flash point was measured in only one upgraded oil and was found to be 37°C. However, no conclusions can be drawn from this one data point. We do not have comparable flash point data for crude oil.

4.9 CONRADSON CARBON RESIDUE

Conradson carbon residue (CCR) is an indicator of the likelihood of deposit formation during heating in refinery processes or in fuel handling leading up to combustion. Refiners desire crudes with lower CCR because they leave less residue in reactors. CCR was found to be lower in treated pyrolysis oils than in raw ones. Crude oils have lower CCR than either raw or treated pyrolysis oil. These differences are

illustrated in Fig. 19 below. Only a few studies measured CCR in either raw or treated pyrolysis oils. This is an important variable when considering coprocessing at refineries, so future studies should investigate CCR in pyrolysis oil.

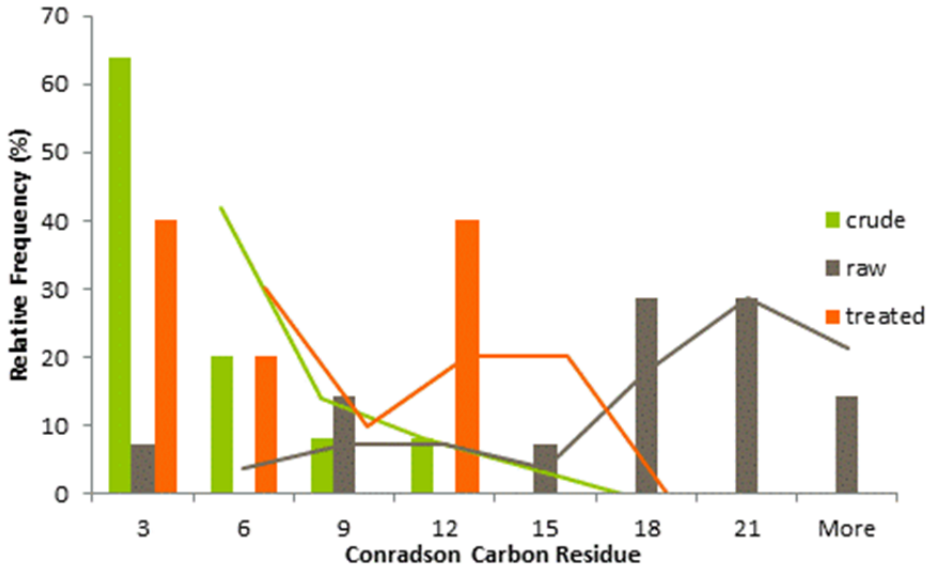

Fig. 19. Conradson carbon residue in crude oil, raw pyrolysis oil, and treated pyrolysis oil. Lines show 2-point moving averages.

5. PROCESS VARIABLES

5.1 REACTOR TYPE

The primary types of pyrolysis reactors used in the references for this study were vacuum, rotating cone, vortex, fluidized bed, and fixed bed. Vacuum reactors operate at pressures between 1 and 10 kPa and are designed to reduce the formation of solid products. Some vacuum reactors are screw-fed, while others utilize multiple-hearth systems. Rotating-cone reactors use centrifugal force to propel biomass and sand up and out of a rotating cone using no carrier gas. The lack of carrier gas should allow for easier recovery of liquid products. Vortex reactors heat biomass by ablation, meaning that the biomass moves across a heated surface in the reactor, which pyrolyzes the outer layers of the biomass first. Fluidized-bed reactors use a carrier gas to fluidize the biomass and sand, which assists in heat transfer (9). Fixed-bed reactors generally use packed beds, where a sweep gas flows through a tube-shaped reactor with a packed bed of biomass (52). Pyrolysis reactors, which were not well described or did not fit in one of these categories, were not included in this portion of the analysis.

There is a wide range of data for oils obtained from each type of reactor, and it appears that each reactor type can be operated in such a way as to produce high- or low-quality oils. However, it does appear that some reactor designs consistently yield more liquid or char. The fluidized-bed reactor design tends to yield more liquid than fixed-bed reactors or vacuum pyrolysis reactors, with an average yield of 60.3% liquid for the fluidized bed compared to 57.3% for fluidized beds and 50.0% for vacuum pyrolysis processes. ANOVA analysis gives only a 9.3% probability that these differences in mean yield are caused by random error. Differences in char yield have also been seen between fluidized- and fixed-bed reactors. The fluidized bed yields an average of only 17.3% char, while the fixed bed yields an average of 27.3% char. A two-tailed T-test gives only an 8.8% probability that these differences in mean yield are caused by random error. Hence it appears that a fluidized-bed reactor may be a better choice for biomass pyrolysis. These differences in yield can be seen in in Figs. 20 and 21.

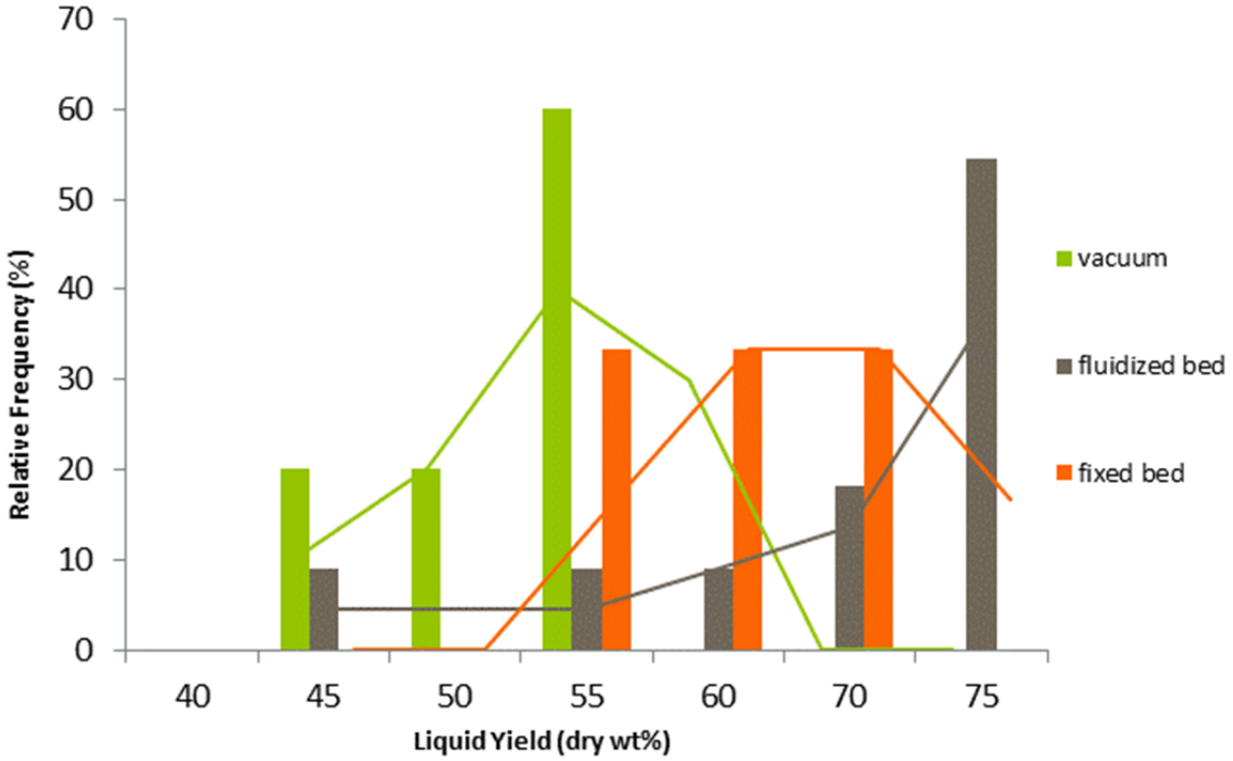

Fig. 20. Liquid yields of different reactor types.

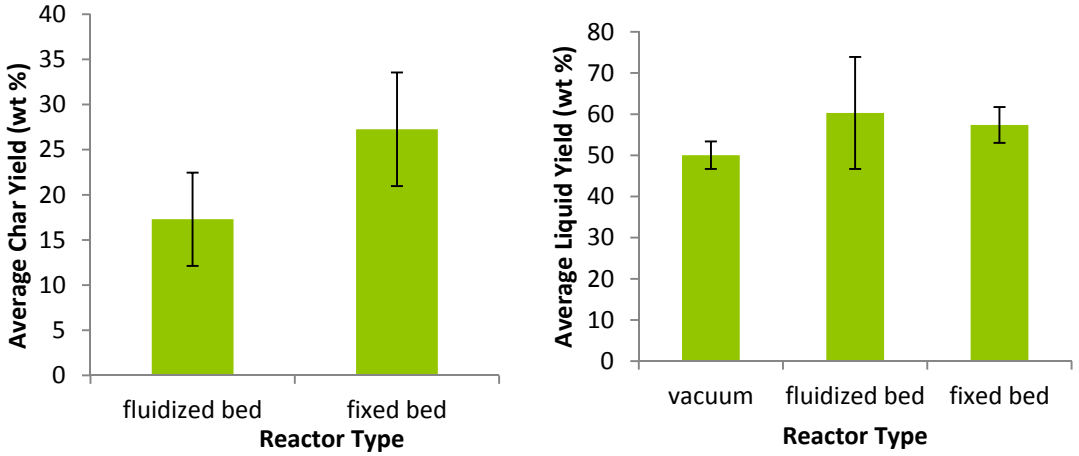

Fig. 21. Differences in liquid and char yields of different reactor types.

5.2 FEEDSTOCK

The pyrolysis oil samples described in our database are derived from a variety of feedstocks. These feedstocks have been classified into four categories for our analysis: hardwoods; softwoods; nuts, seeds, and their residues; and crop residues. Pyrolysis oils for which feedstock was not well described or did not fit into one of these categories were not included in this portion of the analysis. Table 4 shows average values for the properties discussed in this report for each of these categories. Because of the high variability in the data, many of the differences between oils from different feedstocks are not statistically significant. However, several that are significant are discussed below.

Table 4. Average values of chemical and physical properties for raw pyrolysis oil derived from different feedstocks

	Softwood	Hardwood	Nuts, seeds, and nut and seed residues	Crop residues
Specific gravity	1.202	1.189	1.050	1.160
API gravity	-13.66	-12.32	4.28	-8.74
Viscosity at 40C	37.81	37.88	49.63	40.13
pH	2.7	2.6	4.8	3.1
TAN	72.25	108.80		107.65
Pour point	-21	-32	-18	-16
Flash point	77	66	88	90
Ash	0.10	0.08	0.01	0.08
CCR	18.25	16.15		20.80
Solids	0.24	0.15		0.23
% water	22.22	23.21	20.22	19.88
% H as-received	7.12	7.39	9.80	7.40
% O dry	37.88	37.36	26.90	31.62
% O as-received	45.52	48.87	33.42	41.22
% C as-received	48.80	44.34	59.01	50.09
% N as-received	0.41	0.18	1.10	1.10
% S as-received	0.04	0.03		0.09
HHV as-received	20.34	19.64	19.25	21.96
H/C dry	1.42	1.35	1.73	1.35

Several important differences were seen between pyrolysis oils derived from different feedstocks. First, pyrolysis oils derived from crop residue appear to have lower oxygen content, higher pH, and higher heating values than pyrolysis oils derived from either softwood or hardwood. Second, nuts, seeds, nut residues, and seed residues appear to produce lighter pyrolysis oil with greater hydrogen contents and higher H:C ratios than either softwoods, hardwoods, or crop residues. This may be a product of original feedstock composition. Nuts, seeds, and their residues tend to have higher fatty acid contents than other feedstocks. Finally, softwood pyrolysis oils have lower TAN than hardwood oils. This was the only significant difference seen between softwood and hardwood pyrolysis oils. These relationships can be seen with p-values in Fig. 22.

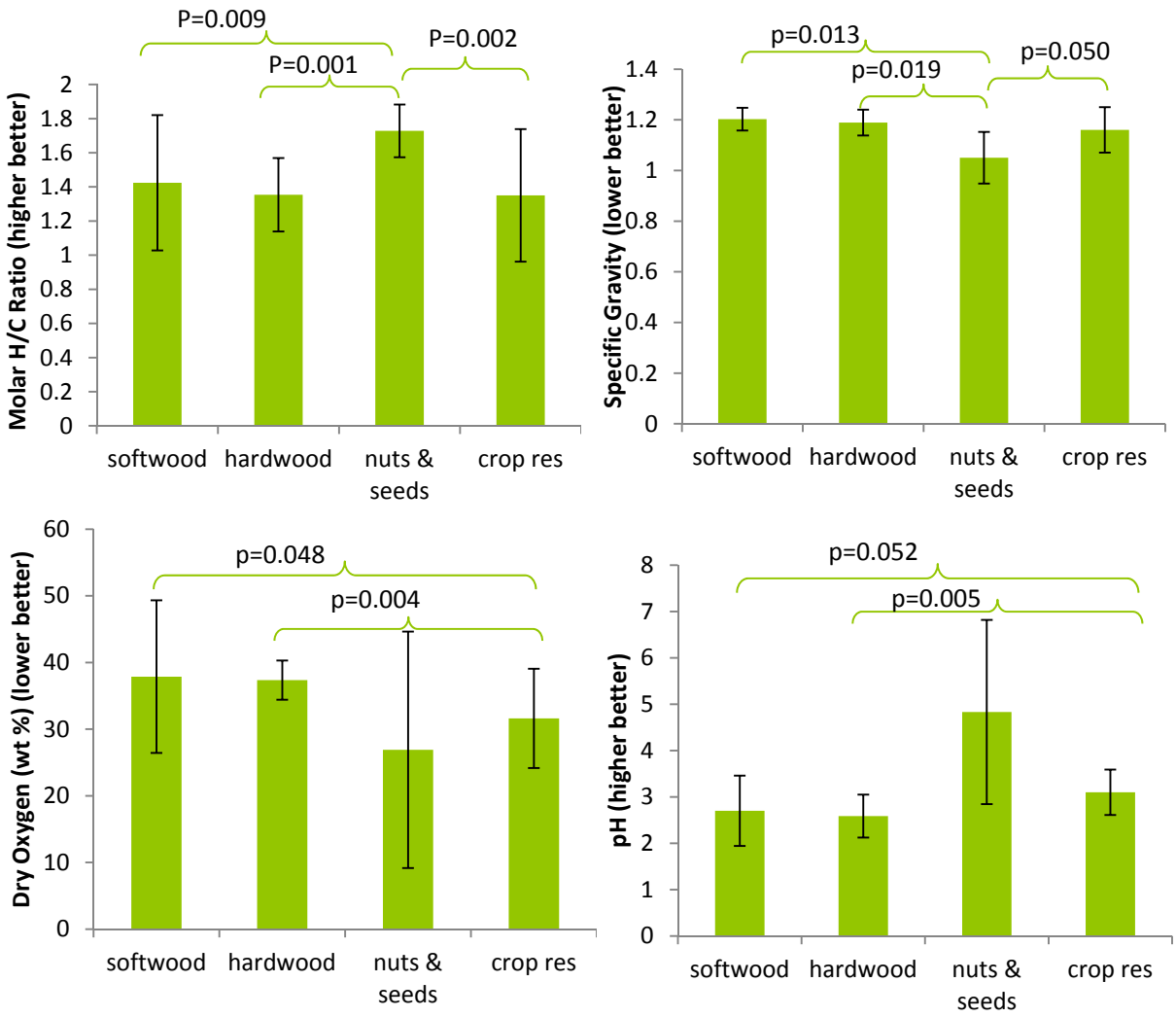

Fig. 22. Pyrolysis oil quality measures based on feedstock.

5.3 METHOD OF UPGRADING

The studies represented in our database used five different methods to upgrade pyrolysis oil: hydrotreatment, zeolite cracking, esterification with alcohol, and catalytic pyrolysis. Hydrotreatment uses catalysts and hydrogen gas to replace heteroatoms with hydrogen atoms and to saturate unsaturated hydrocarbons. This process is similar to that used to remove sulfur from and to upgrade crude oil. Hydrotreating processes were broken into two subgroups: those that used alumina-supported catalysts, and those that used carbon-supported catalysts. Zeolite cracking uses zeolite catalysts to break large molecules into smaller ones. Esterification techniques use solid or aqueous acid catalysts to catalyze esterification reactions between carboxylic acids in the pyrolysis oil and alcohols that are mixed with the oil. In catalytic pyrolysis, catalysts are added to the pyrolysis reactor when biomass is first converted to raw pyrolysis oil.

Of these five methods of upgrading pyrolysis oil, hydrotreatment with carbon-supported catalysts appeared to be the most effective. This process produced oils with the lowest water content, highest heating value, and highest pH. Although it was unclear whether hydrotreating processes with carbon- or alumina-supported catalysts produced oils with lower dry oxygen contents, both produced oils with lower

oxygen content than catalytic pyrolysis. In addition to having high oxygen content, oils produced by catalytic pyrolysis had lower heating values than other upgraded oils. These trends are illustrated in Fig. 23.

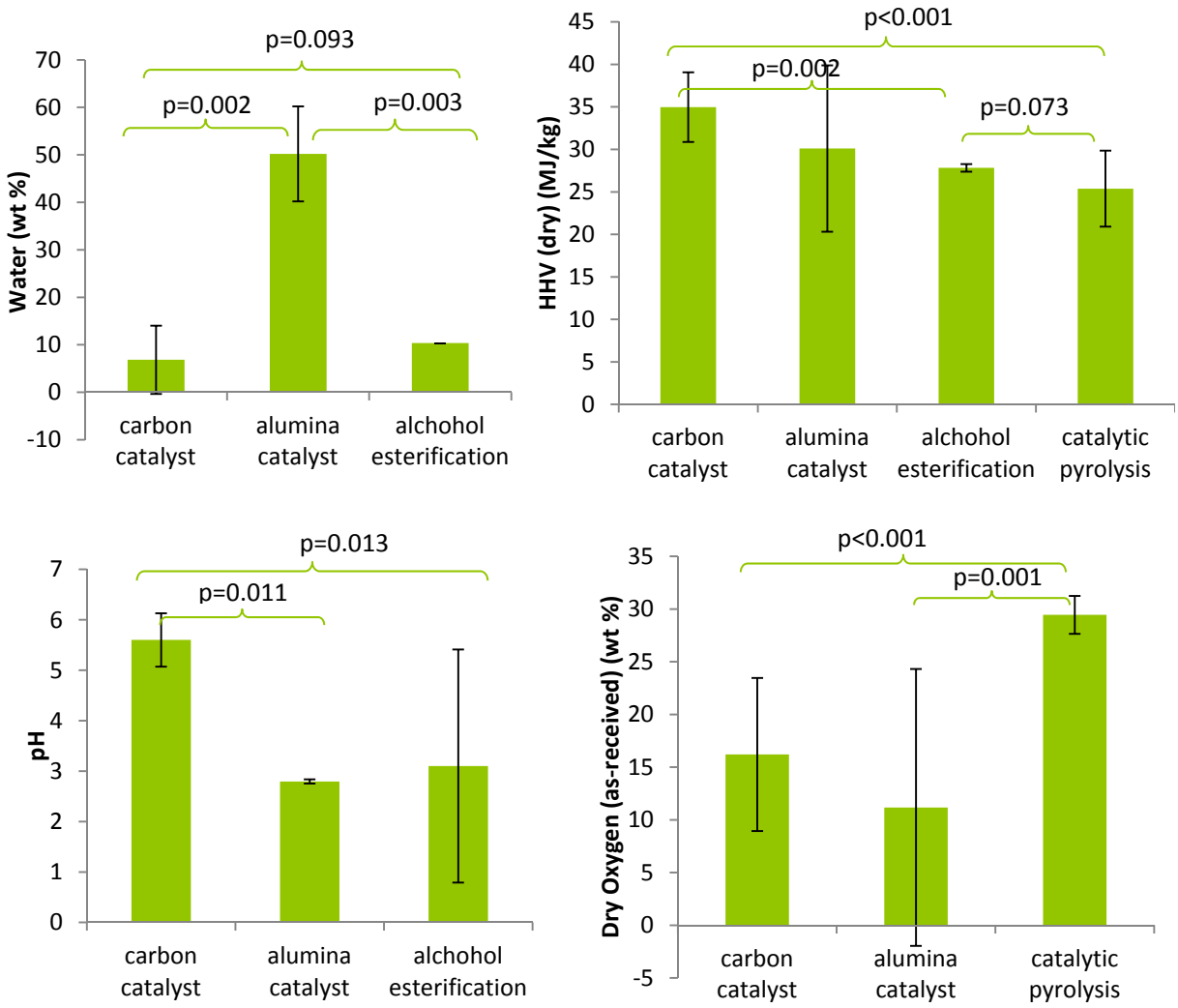

Fig. 23. Comparison of oil quality after different treatment methods.

The only upgrading process for which there was enough data to investigate the effect of process conditions was hydrotreatment. This investigation of the effect of process conditions on oil quality looked at oils subjected to hydrotreatment processes with either carbon- or alumina-supported catalysts as one group. One of the processing conditions that most affected output oil quality was the number of steps in the process. Some hydrotreating processes used in the studies in our database involved two steps, while others involved only one. In some cases, pyrolysis oils were hydrotreated, then an aqueous phase was removed, and then the oil phase was hydrotreated again. In other cases, pyrolysis oils were mixed with a catalyst and brought to a lower temperature for a period of time, then brought to a higher temperature and held for a time. Processes like these were compared with one-step hydrotreating processes and were seen to produce significantly higher quality oils. Oils treated in two-step hydrotreating processes had lower oxygen contents, lower water contents, higher heating values, lower specific gravities, and higher pHs than oils treated in one-step processes. Comparisons of these properties are presented with p-values in Fig. 24. Two-step hydrotreating processes also consumed significantly more hydrogen and had

significantly lower yields than one-step processes, which makes them more expensive. These properties are compared in Fig. 25. The inverse relationship between yield and quality and the direct relationship between hydrogen consumption and quality are generally not present when we look within the subgroup of one-process oils. The only correlation seen with either yield or hydrogen consumption within the group of one-process oils was between heating value and hydrogen consumption. Although this was a very strong correlation, only six data points from two studies had the necessary data to contribute to the correlation, so it may not be representative of all pyrolysis oils that have been upgraded with one-step hydrotreatment. The lack of data for this correlation could also explain why hydrogen consumption could correlate with heating value, but not with oxygen, water, or acidity. This correlation between hydrogen consumption and heating value can be seen in Fig. 26.

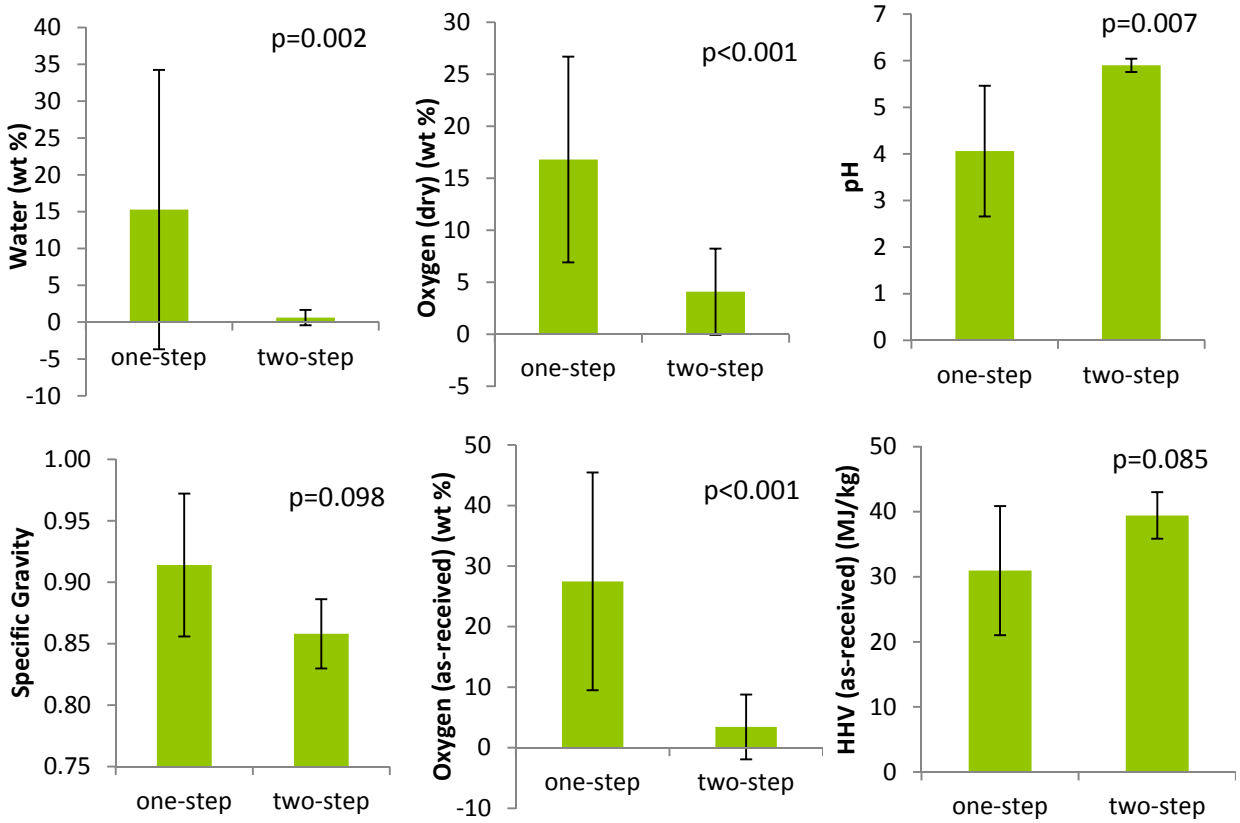

Fig. 24. Improved qualities of oils treated with two-step hydrotreatment processes compared to one-step hydrotreatment processes.

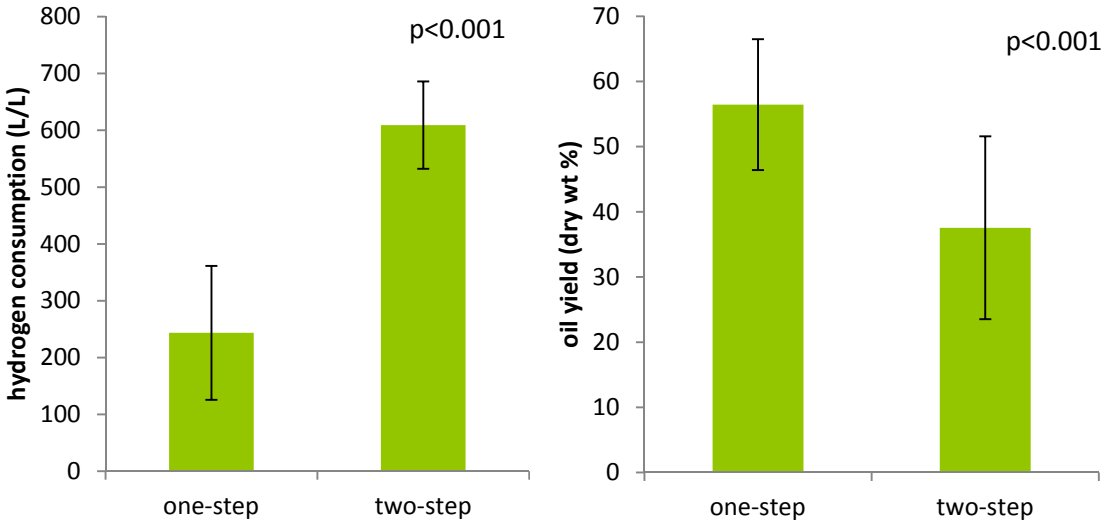

Fig. 25. Process characteristics for one- and two-step hydrotreatment processes.

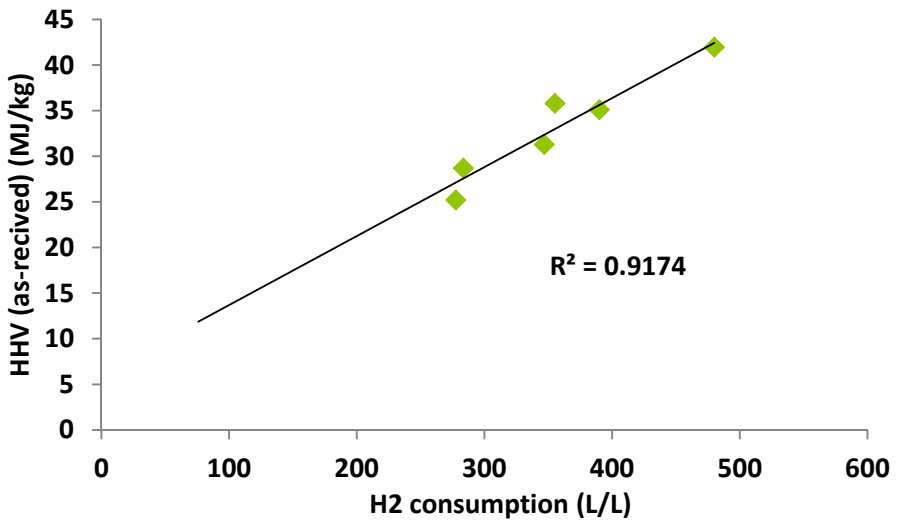

Fig. 26. Hydrogen consumption and heating value.

Within the group of oils subjected to one-step hydrotreatment, there is a relationship between oil quality and hydrotreating temperature. Higher temperatures promote more chemical reactions, leading to higher quality oils. Figure 27 illustrates the correlations between temperature and heating value, oxygen content, and water. We were not able to compare the effect of temperature on two-step hydrotreatment processes because these processes did not use a single temperature**.**

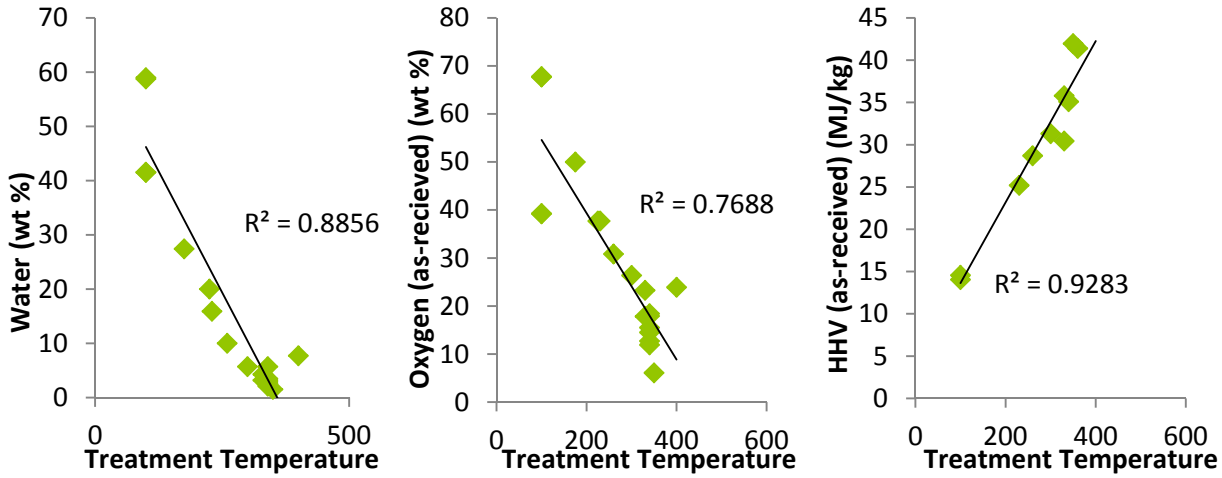

Fig. 27. Improvement in oil quality with increasing temperature.

Another area that was investigated was the relationship between oil quality before and after treating. There did not appear to be significant correlations between the water or oxygen content before hydrotreatment and the quality of the upgraded oil. It does appear that raw oils with higher oxygen content consume more hydrogen during hydrotreatment. This relationship is shown in Fig. 28. This suggests while it may be possible to upgrade raw pyrolysis oils of any quality using hydrotreament, upgrading lower quality oils will require more hydrogen. This may make upgrading low-quality raw oils more expensive and would increase the importance of designing pyrolysis processes to produce the highest quality raw oil possible. The expense of hydrotreating low-quality oils could also favor two-step upgrading processes where the first step is not hydrotreatment, although such processes might trade lower yield for lower hydrogen consumption.

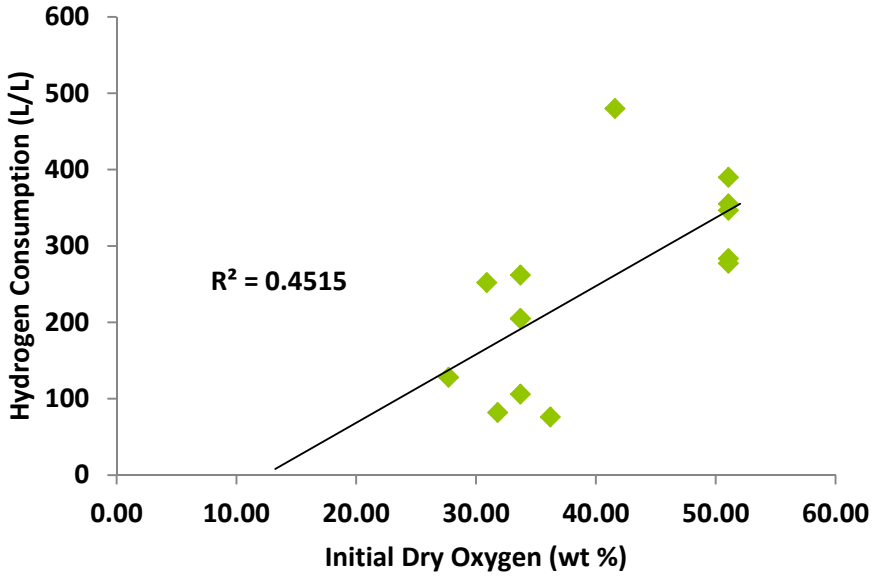

Fig. 28. Hydrogen consumption increasing with the oxygen content of raw pyrolysis oil.

Hydrogen gas is expensive, and its consumption during hydrotreatment raises the cost of upgrading pyrolysis oil. However, when the chemistry of pyrolysis oil is examined, it is clear that significant hydrogen consumption is necessary to improve oil quality. We calculated the theoretical quantity of

hydrogen that would be consumed in improving average raw pyrolysis oil to pipeline shipment quality. Based on our database, average raw oil was deemed to be 22% water and 34% oxygen on a dry basis, and to have a molar H:C ratio of 1.39 and a specific gravity of 1.2. The target upgrading level was set at 0% water, 2% oxygen, and 1.8 H:C ratio. We consider 2% oxygen on an as-received basis to be similar to 2% water, and 1.8 H:C is an average for crude oils. To calculate the theoretical hydrogen consumption for this process, it was assumed that all water was "free water" and could be removed without hydrogen consumption. Further, it was assumed that all oxygen in hydrocarbons could be removed using two hydrogen atoms. This assumption was based on the fact that during hydrodeoxygenation, oxygen atoms react with hydrogen to form water, and the oxygen on the hydrocarbon is often replaced by hydrogen that was previously bound to the now removed oxygen. However, many other reactions occur during hydrotreatment, which limit this assumption. For example, carboxyl and carbonyl groups can be removed without the addition of hydrogen as CO_2 and CO, respectively. Phenol and furan groups often must be hydrogenated and/or cleaved before oxygen can be removed, increasing hydrogen consumption. Using these assumptions, we determined that 674.5 L of hydrogen gas per liter of as-received oil (822.9 L of hydrogen gas per liter of oil (dry) or 6.12 wt %) must be consumed in upgrading this average raw oil to pipeline quality. Hydrogen consumptions recorded in our database ranged from 75 to 710 L/L (basis not specified). Within the subgroup of processes that produced pipeline-quality oils, hydrogen consumption was between 490 and 710 L/L (basis not specified).

Both theoretical and experimental hydrogen consumptions are far higher than the predicted hydrogen consumption in hydrotreatment processes for crude. The hydrotreatment of crude focuses on removal of sulfur instead of oxygen. We calculated hydrogen consumption for upgrading of the dirtiest crude in our crude database, which was 4% sulfur and had an H:C ratio of 1.62. The upgrading target for this oil was 0% sulfur and 1.82 H:C ratio. It was assumed that two hydrogen atoms were required to remove each sulfur atom. We calculated that it would require only 170 L/L hydrogen consumption to completely upgrade this dirtiest oil. An average crude oil, which is only 0.48% sulfur and already has a H:C ratio of 1.82, would only require hydrogen consumption of 3 L/L. So, although catalysts can be developed to minimize hydrogen consumption in hydrotreatment of pyrolysis oil, this process will always require much more hydrogen than hydrotreatment of crude oil in order to produce hydrocarbon oils.

6. PIPELINE LOCATIONS

Assuming that pyrolysis and upgrading processes are improved to the point that pyrolysis oil can be transported by pipeline, there is still an important logistical problem concerning the adjacency of pipelines and biomass resources. Although more than 42% of the counties in the United States contain a pipeline of some kind, only a small portion of these contain either a crude oil collection system or an intrastate crude pipeline. Only 381 counties, just over 12% of the total, contain either a crude oil collection system or an intrastate crude pipeline. Of these 381 counties, 129 counties contain both crude gathering and intrastate pipelines, 216 contain only intrastate crude pipelines, and 36 contain only crude gathering systems. These pipeline resources are presented visually on the map in Fig. 29. Thus, even before biomass resources are considered, it is clear that only a small portion of counties will be potential pyrolysis oil plant sites for the criteria of this study. Our pipeline database was generated in 2011 and used for all projections to future years. However, new pipelines may be added in states where fracking is being practiced for increased natural gas or oil production, and these areas should be reevaluated for pipeline potential in future studies.

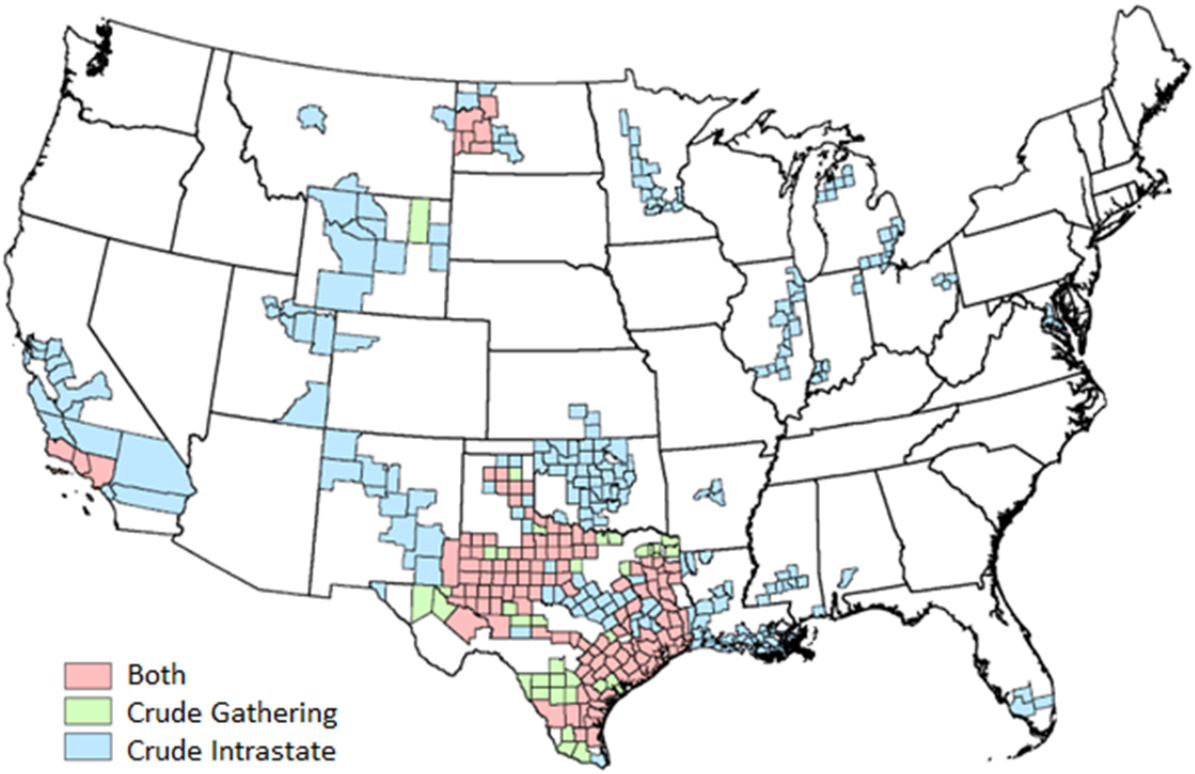

Fig. 29. Counties with crude gathering systems, intrastate crude pipelines, or both.

Intrastate LPG and natural gas liquids pipelines are also a limited resource. These were not considered to be a requirement in this study but may be useful for shipping light materials generated during pyrolysis upgrading. In total, 265 counties have either intrastate LPG or natural gas liquids pipelines, or both. Of these, 26 have intrastate LPG pipelines, 185 have intrastate natural gas liquids pipelines, and 54 have both. There is significant overlap between counties with intrastate and gathering crude pipelines and those with intrastate LPG and NGL pipelines, with 163 counties having at least one type of pipeline from both of these categories. These counties are potentially more important because intrastate or gathering crude pipelines could allow for transportation of bio oil, while intrastate LPG or natural gas liquids pipelines

could allow for transportation of low-molecular-weight products. The presence of both of these categories of pipeline would allow for the shipping of a larger portion of products than if only intrastate or gathering crude pipelines are present.

The state with the highest percentage of counties with intrastate or gathering crude pipelines is Texas, where 73.23% of counties have at least one of these types of pipeline. Further, 41.73% of counties in Texas have both an intrastate or gathering crude pipeline, and an intrastate LPG or NGL pipeline. Other states with high potential, listed in order of decreasing potential, include Oklahoma, Wyoming, New Mexico, Louisiana, California, Utah, and North Dakota. More than 20% of counties in these states contain intrastate or gathering crude pipelines.

Most states have few or no counties with intrastate or gathering crude pipelines. There are 26 states with zero intrastate or gathering crude pipelines. These states are located across the country, but are particularly prevalent along the East Coast.

In addition to pipeline resources concentrated in states like Texas, California, North Dakota, New Mexico, and Oklahoma and associated with the production of domestic crude oil, stretches of pipeline are also present in regions with no oil production. These include Minnesota, Maryland, northwestern Ohio, and northern Indiana. In these areas, intrastate pipelines are used to transport oil from storage facilities and receiving points to refineries or power stations. These pipelines are either fed by crude from Canada that has been shipped to the storage facility via a larger pipeline, or by crude arriving at nearby ports from domestic and foreign sources.

7. BIOMASS RESOURCE LOCATIONS

Biomass resources are more widely available than crude pipelines. There are adequate biomass resources for a pyrolysis oil plant in 78.60% of counties in 2012 and in 88.84% of counties by 2030. Along with this 13% increase in counties having a critical density of biomass, the total quantity of biomass increases 3.36-fold from 200 to 675 million dry tons per year over this time period. This increase is largely in counties that could already support pyrolysis plants. In 2012, 96.2% of all biomass was produced in counties with biomass density above the 18.6 dry tons/acre/year threshold, and by 2030, 99.1% will be produced in counties with biomass density above this threshold. Although the biomass increase seen between 2012 and 2030 opens only a few new counties as potential pyrolysis plant sites, the overall increase is still important because it could lead to larger and more profitable plants or to shorter transportation distances. Figures 30 and 31 show the frequency distribution of county biomass density levels during 2012, 2022, and 2030, indicating many times greater biomass density than our minimum threshold of 18.6.

The major factor in the increase in biomass density is the development of energy crops. Energy crops, which are not commercially present in 2012, are projected to make up nearly 60% of all available biomass by 2030. Their emergence is responsible for 84.25% of the total increase in biomass. The dominant energy crops are perennial grasses, which make up 66.73% of this sector in 2022 and 63.81% in 2030. Woody crops comprise 29.86% of energy crops in 2022 and 31.45% in 2030, and the annual energy crop sorghum makes up 3.45% of the energy crop biomass in 2022 and 4.73% in 2030. This energy-crop-driven increase can be seen in Fig. 32.

Secondary residues and wastes play a notably small role in the country's biomass resources. They make up only 16.73% of all biomass in 2012, and this contribution drops to 5.51% by 2030. This is largely because these resources are already being used today.

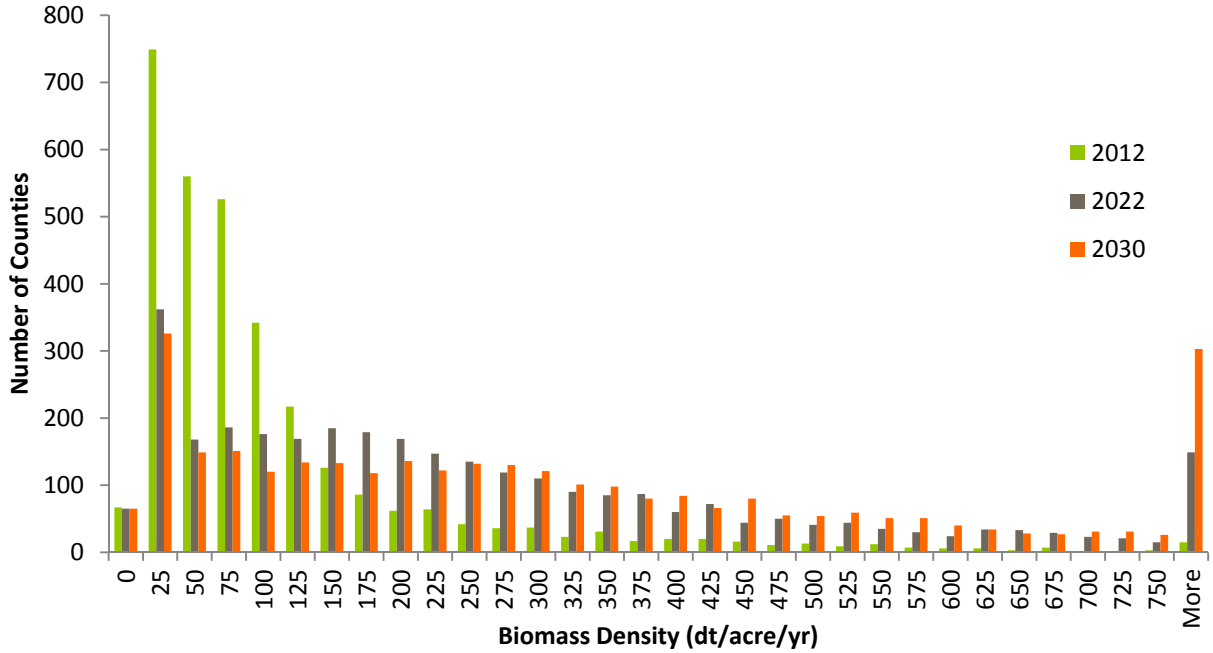

Fig. 30. Number of counties with various levels of biomass density in 2012, 2022, and 2030.

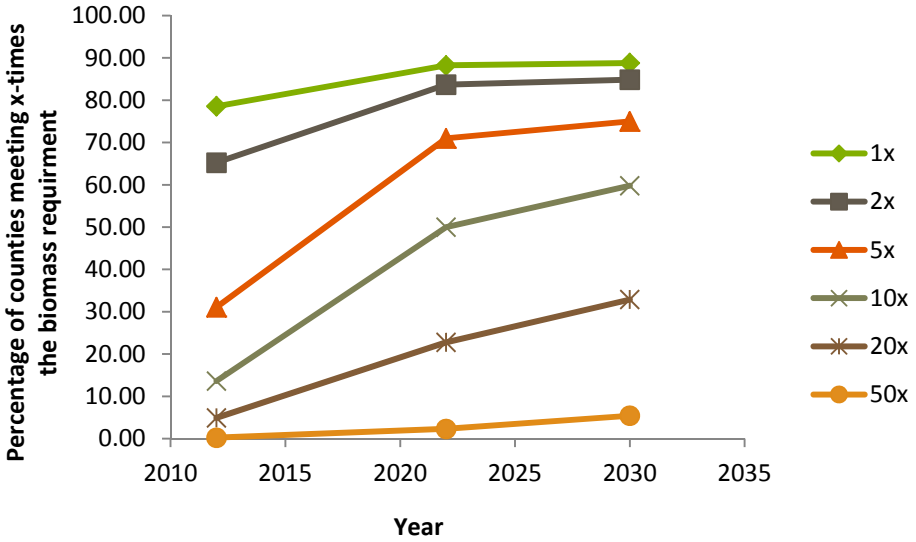

Fig. 31. Percentage of counties meeting *x*-times the minimum biomass density requirement of 18.6 dry tons/acre/year.

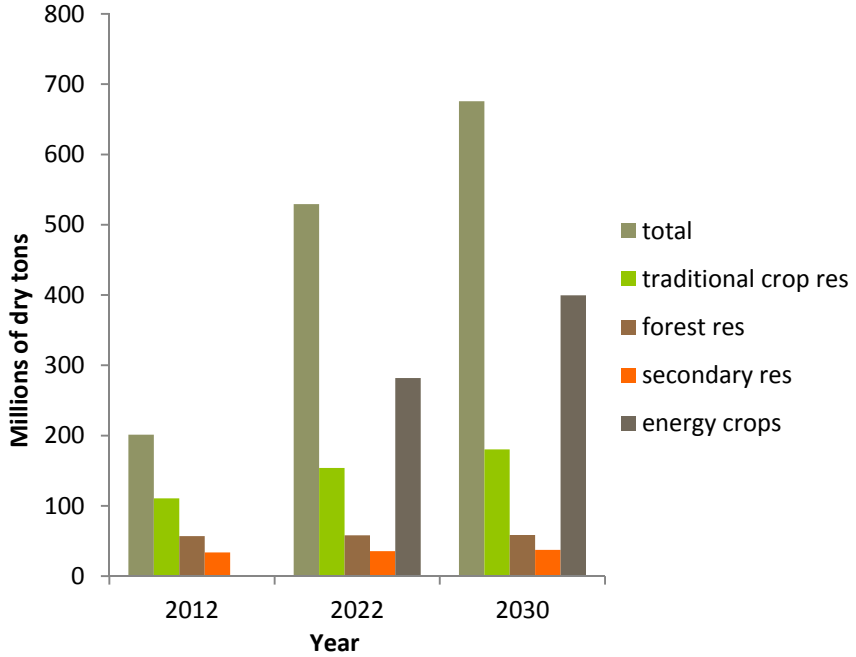

Fig. 32. Biomass resources by type.

In 25 states more than 90% of counties have sufficient biomass resources to support a pyrolysis plant in 2012. This increases to 31 states by 2030. These states are well distributed across most of the United States. There are only eight states where less than 50% of counties have the biomass resources to support a pyrolysis plant in 2012, and this number decreases to six by 2030. These low-potential states are all located in the mountainous West and Southwest where biomass growth is limited by the availability of water. The two states that become significantly more productive over time and pass this 50% mark are Texas and Oklahoma. This development is especially important because these states also have high pipeline density. Even in the arid states where less than 50% of counties produce enough biomass to

support a pyrolysis plant, there still is significant biomass production in some counties, and there are areas where biomass resources are plentiful. The increase in counties meeting minimum biomass requirements is illustrated in Fig. 33. Figure 34 shows the projected distribution of biomass across the United States in 2030. It is important to note that in most regions of the United States, the growing season is not 12 months long, and technology must be available for crop storage in order to support year-round operation of a biomass pyrolysis plant. This could involve a silo or elevator storage system, storage in the field, or some other form of storage.

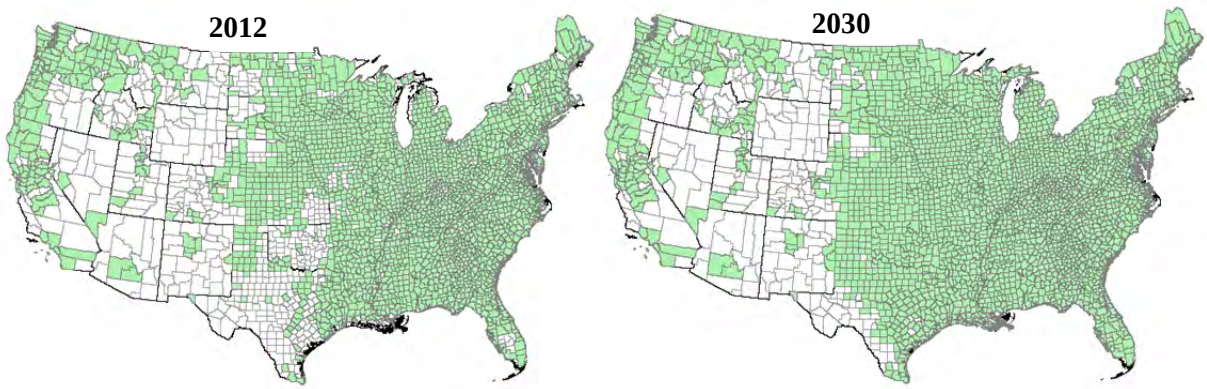

Fig. 33. Maps of counties meeting the 18.59 dry tons/acre/year requirement in 2012 and 2030.

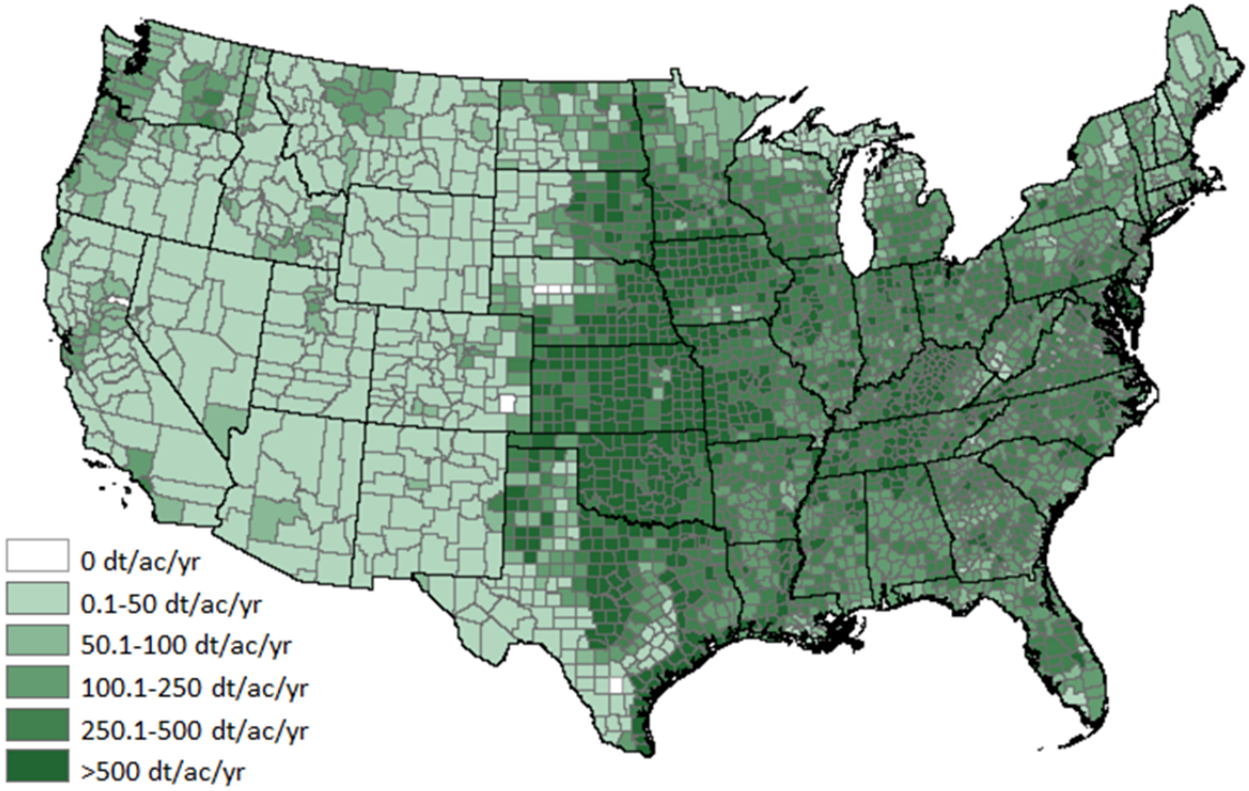

Fig. 34. Projected biomass density by county in 2030.

8. ADJACENCY OF BIOMASS AND PIPELINE RESOURCES

Despite their concentration in different regions of the country, pipeline and biomass resources show some overlap. There are 181 counties that will meet both biomass and pipeline requirements in 2012, and 314 that will meet them in 2030. This is equal to 5.8% of all counties in 2012, and 10% in 2030. This model of biomass conversion through pyrolysis and shipment by pipeline would allow access to biomass resources in these counties accounting for 7.4% of total unused biomass in 2012 and 18% in 2030. This biomass could produce 29.9 million barrels of petroleum equivalent per year in 2012, and 243.2 million barrels of petroleum equivalent per year in 2030. Based on 2010 petroleum usage estimates of 19.15 million barrels per day (53), pyrolysis oil produced under the model described in this report could replace 0.43% of petroleum in 2012, and 3.48% in 2030. These numbers may appear low compared to other estimates of biomass potential but include the requirement of adjacency of biomass and pipelines and are based only on new, not currently utilized, biomass resources. Hence transportation of pyrolysis oil by existing pipelines could play a major, but not complete, role in biomass utilization.

With the assumptions of this study, pipeline presence is usually the factor that prevents a county from being appropriate for a pyrolysis plant. In 2012, 7.3% of counties that meet biomass requirements also meet pipeline requirements. This jumps to 11.3% in 2030. This 1.5-fold increase in the percentage of counties with more than 18.6 dry tons/acre/year of biomass that also have appropriate pipelines is due to marginal biomass counties with pipelines crossing our biomass threshold as a result of improved crop yield and the emergence of energy crops. Specifically, 41.4% of counties that reach the minimum biomass requirement between 2012 and 2030 have pipelines, which is significantly above the 2012 7.3% national rate of counties with critical biomass density that have pipelines. The comparison between the number of counties that meet biomass requirements, the number of counties that meet pipeline requirements, and the number of counties that meet both requirements can be seen in Fig. 35. This figure also illustrates the significance of the increase in counties with necessary biomass and pipeline resources compared to that of the increase in all counties with necessary biomass. Statistics related to biomass and pipeline requirements are summarized in Table 5.

In 2012, Texas and Louisiana are the only states where more than 20% of counties meet both biomass and pipeline requirements (26.0% in Texas and 23.4% in Louisiana). By 2030, increasing biomass resources have pushed Oklahoma and California into this range too. Texas still has the greatest percentage of counties with both appropriate biomass and pipeline resources, which has now more than doubled to 61.4%, and Oklahoma is second with 46.8% of counties having appropriate resources, more than four times as many as in 2012. Other states with more moderate potential, where between 10 and 20% of counties have both biomass and pipeline resources in 2030, listed in order of decreasing potential, include Minnesota, Michigan, Illinois, Maryland, North Dakota, Mississippi, and Utah.

Areas of notably low potential are the same as those mentioned previously as having no pipeline resources and are located along the East Coast. Additionally, the mountainous or arid western states of Wyoming, Colorado, and New Mexico have no counties that meet both requirements, despite having pipeline resources, because of their poor suitability for biomass growth.

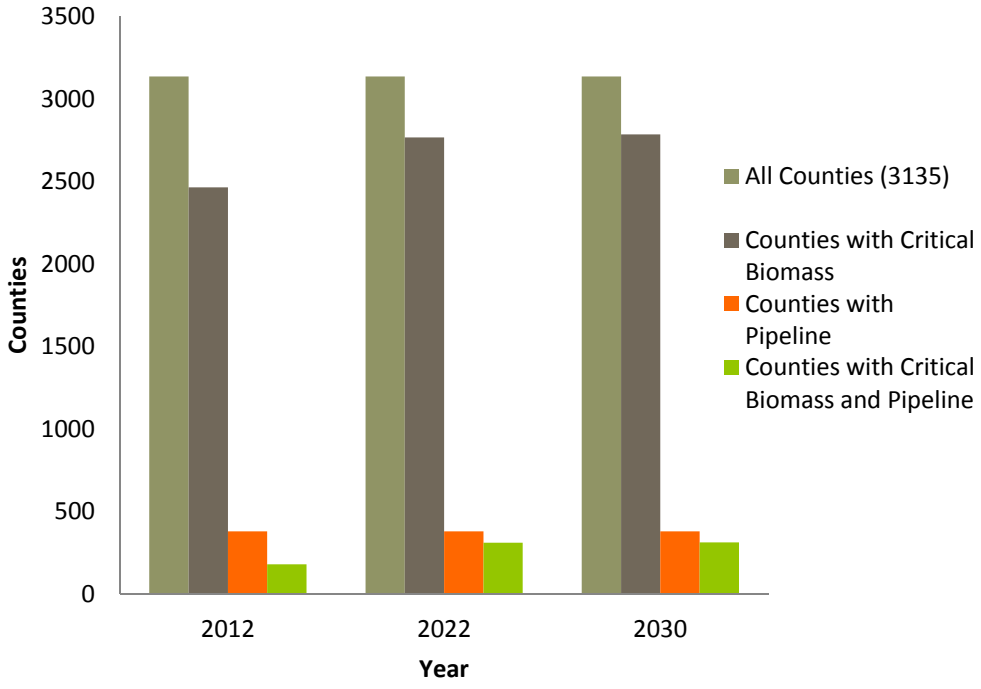

Fig. 35. Counties with the biomass or pipeline resources needed for a pyrolysis plant.

Table 5. Statistics on overlap of pipeline and biomass resources (%)

Percentage of	2012	2022	2030
All counties meeting biomass requirement	96.19	98.88	99.14
All counties meeting pipeline requirement	12.5	12.5	12.5
Counties meeting biomass requirement that also meet pipeline requirement	7.35	11.28	11.27
Counties meeting pipeline requirement that also meet biomass requirement	47.51	81.9	82.41
All counties meeting both requirements	5.77	9.95	10.02
All biomass accessed via this analysis	7.41	16.25	18.00
Petroleum replaceable under model	0.43	2.46	3.48

9. CONCLUSIONS

In conclusion, the model of shipping pyrolysis oil by pipeline to oil refineries for process heat or further refining could play an important role in utilizing biomass resources. However, it cannot access all biomass resources and is limited by technical problems related to chemistry, compatibility, and upgrading requirements. From a logistical standpoint, this model can access 7.4% of total unused biomass in 2010 and 18% in 2030. States where this model works particularly well are Texas, Oklahoma, California, and Louisiana. In these states, this model accesses 75.1%, 56.7%, 41.5%, and 26.8% of biomass resources, respectively.

Some states with minimal or no existing pipelines are currently undergoing extensive drilling and development for enhanced natural gas and oil recover. This development may result in new pipelines being co-developed to support both crude oil and pyrolysis oil resources.

Even when biomass can be accessed by this model, significant upgrading will be needed to bring pyrolysis oils to a quality acceptable for pipeline transport. We have translated the 2% water and sediments specification given by most pipeline operating companies and regulating agencies into a 2% oxygen requirement. Only one of the 43 sources included in our database produced pyrolysis oil that had less than 2% oxygen on an as-received basis. The upgrading process used in this study, two-step hydrotreatment, was consistently the most effective upgrading method for pyrolysis oil. However, it also showed higher hydrogen consumption and lower yield than other processes, making it less economical.

There is great need for further research on the physical properties of pyrolysis oil and how these properties are affected by upgrading. We were unable to find data on pour point or flash point for upgraded oils and were unable to find any data on Reid vapor pressure of pyrolysis oil. These properties are important for safety and handling concerns. Further, trends relating pH, viscosity, and Conradson carbon residue to other oil properties were not apparent. Investigation of these properties would be an exciting area for future research.

It is also very important to consider alternate processing techniques, such as zeolite cracking, catalytic pyrolysis, or esterification methods, which might produce higher quality oils with less hydrogen consumption with a possible trade-off of lower yield. An alternate path for pyrolysis oil upgrading that directly produces an oxygenated fuel blending component equivalent to biodiesel should also be explored.

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