CHAPTER 5

Catalytic Biomass Pyrolysis with Reactive Gases

David C. Dayton,[a]* Kaige Wang,[a] Jonathan E. Peters,[a] and Ofei D. Mante[a]

[a] Energy Technology Division, RTI International, 3040 East Cornwallis Road, Research Triangle Park, NC, USA 27709

*Corresponding contributor. E-mail: ddayton@rti.org

Abstract

Recent research and development efforts are focused on 1) developing catalytic processes to modify the chemical and physical properties of direct liquefaction bio-oil intermediates to better match petroleum processes for biofuel production and 2) developing new processes and catalysts to upgrade bio-oils into biofuels. Techno-economic analyses of these pathways highlight the importance of overall product yield for economic viability of biofuels process options.

The objective this chapter is to provide an overview of recent developments in the basic scientific understanding of and technical developments in direct biomass liquefaction processes that use reactive gases, like hydrogen and carbon monoxide, in combination with selective hydrodeoxygenation catalysts to produce low-oxygen-containing bio-crude. A review of hydrodeoxygenation using model compounds with a variety of catalysts at a range of process conditions provides a mechanistic understanding of deoxygenation pathways. Similar studies using real biomass as a feedstock in micropyrolyzers or small laboratory reactors investigate the impact of reactive gases on bio-crude yields and quality.

5. CATALYTIC BIOMASS PYROLYSIS WITH REACTIVE GASES

5.1 Introduction

Thermochemical conversion pathways can be classified as direct and indirect liquefaction processes that convert biomass into intermediates that are upgraded to biofuels. Direct liquefaction pathways for predominantly dry feedstocks include biomass fast pyrolysis, catalytic fast pyrolysis (CFP) (in situ and ex situ), and hydropyrolysis (HYP) that yield a liquid referred to as bio-oil or bio-crude suitable for upgrading to final fuels. An attractive strategy has been to leverage years of technical development and capital expenditures in the petrochemical industry by adapting crude oil processing technologies for upgrading these liquid intermediates into advanced biofuels. These advanced biofuels are expected to be drop-in hydrocarbon-based intermediates or fuels to replace petroleum liquids in the existing refining and distribution infrastructure.[1-3]

Although bio-oil has prospects for being upgraded in a manner similar to petroleum, the similarities between the two kinds oil ends there. The elemental composition of bio-oil more closely resembles that of biomass than petroleum, and the chemical and physical properties of bio-oil, such as high oxygen content, low pH, and poor thermal stability, are not directly translatable to petroleum processing technologies. Therefore, recent research and development efforts are focused on 1) developing catalytic processes to modify the chemical and physical properties of bio-oil to better match petroleum processes for biofuel production and 2) developing new processes and catalysts to upgrade bio-oils into biofuels. Techno-economic analyses of these pathways highlight the importance of overall product yield for economic viability of biofuels process options.

Biomass pyrolysis is the thermal depolymerization of biomass at modest temperatures in the absence of added oxygen. The slate of products from biomass pyrolysis depends on the feedstock, process temperature, pressure, and residence time of the liberated pyrolysis vapors.

The poor fuel properties of biomass fast pyrolysis oils make it unsuitable for directly integrating into the current petroleum refining infrastructure.[4] Upgrading bio-oil into transportation fuels requires removal of oxygen and an increase in the hydrogen-to-carbon ratio.[5] Therefore, one of the challenges in developing biofuels technologies is efficient utilization of hydrogen while maximizing carbon (energy) conversion efficiency and minimizing oxygen content in the product.

In the past several years, CFP has been explored to improve the quality of liquid intermediates. The role of the catalyst in direct biomass liquefaction processes is to promote deoxygenation of the pyrolysis vapors while minimizing carbon loss to char, light gases, and coke. Oxygen removal during direct biomass liquefaction can occur by dehydration (loss of H_2O), decarboxylation (loss of CO_2), and decarbonylation (loss of CO). Dehydration of the cellulose and hemicellulose fractions during biomass pyrolysis (with or without a catalyst) produces water, referred to as water of pyrolysis, that is the most abundant single component of the liquid phase product. Biomass is inherently oxygen rich and hydrogen deficient, and the catalytic pyrolysis products become even more hydrogen deficient as dehydration occurs, which increases the tendency for aromatic formation and ultimately leads to char/coke production. Deoxygenation by CO and CO_2 removal (decarboxylation and decarbonylation) plus any carbon losses from coke formation on the catalyst lead to lower hydrocarbon liquid yields and lower energy recovery in the bio-crude intermediate.

Numerous researchers have investigated zeolite catalysts for biomass CFP.[5-13] However, hydrocarbon yields from CFP are typically below 20%, while coke yields can be as high as 42% even at optimal reaction conditions in a fluidized bed reactor.[12, 13] Such low carbon efficiency and excessive coke formation have challenged the development of CFP technology for advanced biofuels production.

Many industrial refining processes like hydrocracking, isomerization, and naphtha reforming use hydrogen to control coke formation on the catalyst surface. Consequently, biomass HYP has emerged as a potential solution for maximizing carbon efficiency with improved hydrogen utilization. Biomass HYP involves reacting biomass with hydrogen at elevated temperature and pressure in the presence of a hydrodeoxygenation (HDO) catalyst. Several groups have demonstrated the technical feasibility of producing hydrocarbon-rich liquids from biomass at HYP conditions.[14-21]

One of the technical challenges that faces the continued development of biomass HYP technology is feeding biomass into a high-pressure reactor. Several recent studies have explored the potential of combining the robustness of CFP with the carbon efficiency of biomass HYP by using catalysts optimized for HDO of biomass pyrolysis vapors in hydrogen at atmospheric pressure.[20-23]

The objective of this chapter is to provide an overview of recent progress in the basic scientific understanding of and technical developments in direct biomass liquefaction processes that use reactive gases, like hydrogen and CO, in combination with selective HDO catalysts to produce low-oxygen-containing bio-crude. A review of HDO using model compounds with a variety of catalysts at a range of process conditions provides a mechanistic understanding of deoxygenation pathways. Similar studies using real biomass as a feedstock in micropyrolyzers or small laboratory reactors investigate the impact of reactive gases on bio-crude yields and quality.

5.2 Model Compound Studies

There has been significant effort in recent years to develop catalysts for deoxygenation of bio-oil.[24-26] Many of these studies used model compounds to measure deoxygenation and HDO activity in high-pressure hydrogen.[27-29] Rogers and Zheng[24] have also recently provided a review of deoxygenation studies in low-pressure hydrogen environments covering a wide range of model compounds and catalyst types.

5.2.1 Deoxygenation Reaction Pathways

Many studies typically report on conversion of aromatic oxygenates such as lignin-derived phenolic compounds and holocellulose-derived furanic compounds.[25] One compound that is often studied is the methoxy-substituted phenol guaiacol. It has both phenolic and methoxy functional groups that are commonly found in lignin and lignin derivatives. In general, two main pathways have been identified for the interaction of hydrogen with aromatic oxygenates. The first pathway is hydrogenation (HYD) in which the aromatic ring is first saturated and then oxygen is removed. The second pathway is called direct deoxygenation (DDO) in which oxygen is removed first, followed by aromatic ring saturation. Catalyst functionality is the main factor that drives the reaction toward one pathway over the other.

Petroleum hydrotreating catalysts like bimetallic molybdenum sulfides (NiMo and CoMo) have been tested for bio-oil model compound deoxygenation. In general, molybdenum-based sulfided catalysts tend to favor the DDO pathway.[30, 31] On the contrary, noble metals have been shown to promote the HYD pathway.[27, 28, 32] Catalysts that can selectively promote the DDO pathway without ring saturation are preferred because hydrogen consumption can be minimized.

Another reaction pathway that is observed when catalytically converting methoxy-substituted aromatics is transalkylation and demethlyation by cleavage of the O-CH_3 bond. This pathway has been observed in studies with anisole and guaiacol reacted over various catalysts and is attributed, in part, to the activity of the acidic supports.[33-36] This reaction pathway could be very beneficial for maintaining carbon in the liquid phase instead of losing it as methane in the gas phase. Figure 5.1 shows how guaiacol may undergo DDO and transalkylation reaction pathways to produce methyl-substituted aromatics.

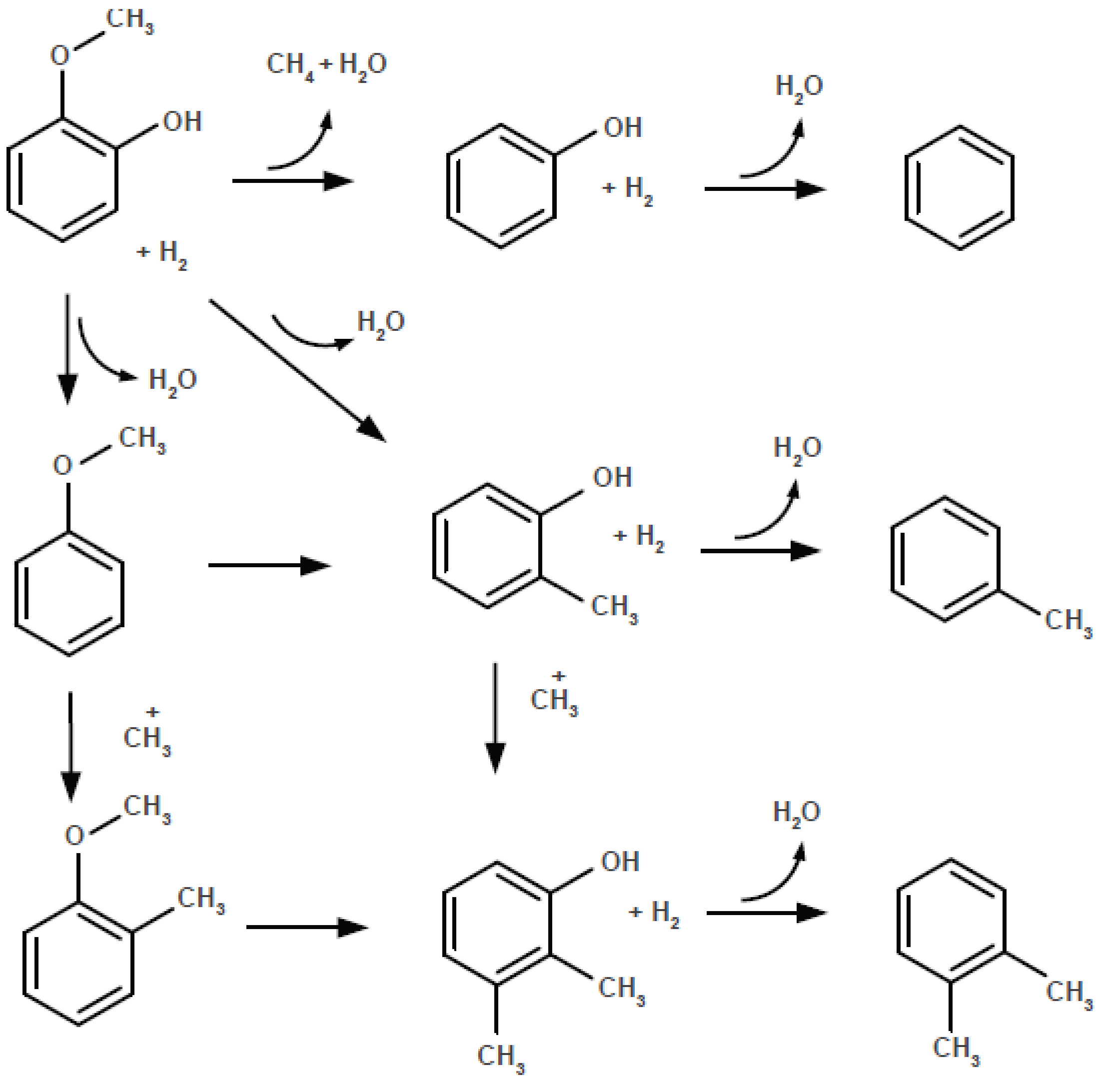

Figure 5.1 Reaction pathways for catalytic hydrodeoxygenation of guaiacol near atmospheric pressure.

5.2.2 Catalyst Development

Conventional sulfided catalysts have typically been evaluated under high-than-atmospheric pressure conditions for bio-oil hydrotreating and usually support the DDO pathway;[32, 37] however, some recent studies have looked at their application under low-pressure conditions to limit hydrogen consumption. Bui et al. measured the promoting effect of cobalt on MoS_2

and reported that it strongly increased the DDO pathway while reducing hydrogenated products at 300°C and 40 bar. [38] Also, there was a significant increase in methylated products with alumina-supported CoMoS versus the unsupported catalyst.[38] Loricera et al. evaluated the effect of sulfided CoMoW supported on mesoporous aluminas SBA-15 and SBA-16 modified with varying amounts of phosphate. It was reported in this case that anisole was converted to mostly phenol and methyl phenols by demethylation and transmethylation reactions promoted by the acidic function of the support; however, very little deoxygenation was observed.[39] Both of these cases indicated significant activity for the transalkyation pathway, but the latter did not suggest significant deoxygenation. The deoxygenation activity may significantly decrease because a sulfur source was not included in the feed to maintain the activity of the metal-sulfide catalysts. The presence of sulfur in the feed stream to maintain catalyst activity presents a drawback to using sulfide catalysts in catalytic pyrolysis applications because the bio-oil feedstocks typically contain very low sulfur compared with the petroleum feedstocks for which these catalysts were designed.

Transition metal oxides have received significant attention for bio-oil deoxygenation. Shimming et al. recently reported that oxygen vacancies in ceria-zirconia catalysts promote DDO of guaiacol to primary products phenol and catechol and secondary products cresol and benzene without significant deactivation after 72 hours.[40] Prasomsri et al. screened several metal oxide catalysts, including V_2O_5, Fe_2O_3, CuO, WO_3, and MoO_3, for HDO near atmosphere pressure.[35] All of these metal oxides investigated were active for HDO to convert biomass-derived oxygenates into unsaturated hydrocarbons but MoO_3 had the highest selectivity to unsaturated hydrocarbons.[41] Shetty et al. also showed that MoO_3 supported on ZrO_2 and TiO_2 has slower deactivation rates caused by coke deposition and could be regenerated by calcining with oxygen at lower temperatures compared to a γ-alumina supported catalyst.[42] The ability to regenerate with oxygen has made supported metal oxides a suitable for catalytic pyrolysis.

Transition metal phosphides are a new class of HDO catalysts that show promise for bio-oil deoxygenation. Zhao et al. compared several transition metal phosphides, including nickel phosphide (Ni_2P), cobalt phosphice (Co_2P), iron phosphide (Fe_2P), tungsten phosphide (WP), and molybdenum phosphide (MoP), on silica support for gas-phase HDO of guaiacol.[43] Ni_2P was found to be the most active catalyst forming mostly benzene and phenol, some anisole but no catechol, and no ring saturation at long contact times. Cresol, which is usually a secondary product, was detected at short contact times. Methylated phenols such as cresol are usually formed via acidic supports, but in this case, Ni_2P could have promoted the transalkylation pathway because metal phosphides can exhibit both Lewis acid sites and metallic functionality.[44] Ni_2P also showed greater deoxygenation activity and stability when compared with commercial Pd/Al_2O_3 and conventional $CoMoS/Al_2O_3$. Wu et al. evaluated the effect of silica, alumina, and zirconia supports for Ni_2P and determined that zirconia promoted the greatest overall deoxygenation activity.[45] Zirconia also increased the demethylation and transalkylation pathways compared with the other supports. Metal phosphides, Ni_2P in particular, are promising catalysts because of their bifunctional nature and their resistance to deactivation.

Recent studies conducted at RTI International investigated the effect of temperature on guaiacol HDO conversion and product selectivity with 2.5 wt% Ni_2P supported on Al_2O_3. Guaiacol vapor in 1 bar of hydrogen was fed over a fixed bed of catalyst at a range of reaction temperatures. Continuous product monitoring during catalyst reduction, guaiacol conversion, and catalyst regeneration provides insights into deoxygenation pathways. The reactor system, analytical methods, and experimental protocols are described in detail in the literature.[46]

Model compound studies for catalytic HDO are typically performed at temperatures between 300 and 400 °C, but catalytic biomass pyrolysis occurs at higher temperatures. Therefore, it is of interest to see how these catalysts perform at temperatures up to 500 °C. Guaiacol conversion and product selectivity from recent experiments conducted at RTI International are provided as a function of temperature shown in Table 5.1.

Table 5.1. Guaiacol conversion and product selectivity for catalytic hydrodeoxygenation of guaiacol over 2.5 wt% Ni_2P on Al_2O_3 at various temperatures under 1 bar hydrogen.

Catalyst	*2.5 wt%Ni_2P/Al_2O_3*				
Temperature (°C)	300	350	400	450	500
Guaiacol conversion (%)	40.1	49.9	71.8	80.7	99.0
Product selectivity (wt% of total products measured)					
Water	3.7	3.0	6.7	9.9	13.7
CO_2	0.0	0.0	0.0	0.0	0.1
Benzene	8.2	8.9	7.0	4.1	4.6
Toluene	6.3	5.9	4.7	2.3	2.4
Phenol	13.8	15.0	24.0	26.1	32.0
Cresol	8.8	10.6	11.4	20.2	20.2
Anisole	7.7	8.8	7.8	4.2	0.1
Methyl-anisole	10.8	13.5	5.7	8.6	9.7
Xylenol	21.3	21.6	22.7	15.1	1.2
CO	2.2	2.4	0.5	0.3	0.0
Methane	0.3	0.4	0.9	2.2	6.5
Coke	16.9	9.9	8.5	7.1	9.5

Guaiacol conversion increased monotonically from 40 to 99% with increasing temperature. The higher concentration of products formed by direct deoxygenation correlates with increased water formation, indicating that hydrogen consumption increased with temperature. Cresol (9 to 20% sel.), xylenol (1 to 23% sel.), and methyl-anisole (6 to 13.5% sel.) were major products, indicating that the transalkylation pathway was also significant. However, there was not a clear trend in methylated products with temperature. Cresol production increased with temperature, xylenol production decreased with temperature, and methyl-anisole production had a minimum at 400 °C. Because both metal phosphide and the alumina support can have active catalytic acid sites, the formation of different methylated products corresponding to the different acid sites may be favored at different temperatures. Overall, the concentration of products from transalkylation reactions is maximized between 400 and 450 °C, while the sequential demethylation reaction is favored at 450 °C and above.

Organic liquid yields from biomass pyrolysis are typically maximized at 500 °C; however, that temperature may not be ideal for catalytic pyrolysis in hydrogen with nickel phosphide supported on alumina if a significant amount of carbon is lost to the gas phase by methane production. Methane selectivity increased from 0.3% at 300 °C to 6.5% at 500 °C. Biomass experiments are required to find the optimum temperature to maximize liquid yield and deoxygenation while minimizing methane production.

Transition metal carbides are also relatively new catalysts that have emerged as potential HDO catalysts for biomass pyrolysis.[47, 48] Wang et al. showed that molybdenum carbide/oxycarbides supported on carbon have higher DDO selectivity than MoP, MoO_2, and MoS_2. However, transition metal carbides are susceptible to irreversible deactivation and are not suitable for catalytic pyrolysis.[49]

Bimetallic catalysts that include an oxophilic metal such as Cu, Fe, and Sn and a noble metal have also been investigated for increased selectivity for the DDO reaction pathway.[34, 50, 51] Sun et al. reported that the bimetallic PdFe catalyst supported on carbon substantially enhanced HDO activity compared with just Pd or Fe alone while also avoiding ring saturation. [51] The Fe is believed to be the active deoxygenation site, while the noble metal activates hydrogen and facilitates deoxygenation as well as Fe reduction. This synergistic effect of bimetallic catalysts is promising; however, noble metals add significant cost to catalyst formulations.

5.3 Biomass Pyrolysis in Reactive Gases

A range of techniques have been applied to understand the impact of adding reactive gases during biomass pyrolysis with and without catalysts. This includes fundamental studies with micropyrolyzers connected directly to the inlet of a gas chromatograph with a mass spectrometric detector (GC/MS) and applied studies that use laboratory-scale reactors (fixed and fluidized beds) to produce limited quantities of bio-crude for analysis and testing.

5.3.1 Batch Pyrolysis: Micro-scale Py-GC/MS Studies

Micro-pyrolzyers coupled with GC/MS (Py-GC/MS) have been used extensively in fundamental research of biomass pyrolysis. Inert gases, including He, Ar, and nitrogen, are typically used as the carrier gas in Py-GC/MS systems. Relatively few Py-GC/MS studies are available that report the influence of ambient and high-pressure reactive gases, especially hydrogen, on biomass pyrolysis and catalytic biomass pyrolysis.

The effect of hydrogen on non-catalytic biomass pyrolysis is minimal, especially at ambient pressure. Studies have shown that the yield of detectable products decreased when hydrogen was added during pyrolysis.[52-54] In addition, the relative concentration of aromatic hydrocarbons increased substantially compared with the results for pyrolysis in an inert atmosphere (helium) and was enhanced with increasing hydrogen pressure.[52-54] Melligan et al.'s[52, 53] work on Py-GC/MS using miscanthus showed that the overall yield of detectable pyrolysis vapors decreased significantly with increasing hydrogen pressure up to 30 bar. Furthermore, the composition of the pyrolysis vapors changed as a function of hydrogen pressure. The most noticeable effect is on the concentration of phenolics and aromatics suggesting that hydrogen plays an important role in lignin thermal decomposition but has a smaller effect on cellulose and hemicellulose thermal decomposition.[52, 53] Another Py-GC/MS study conducted by Resende and co-workers using poplar lignin reported that no aromatic hydrocarbons were observed from Py-GC/MS experiments in He.[55] Helium pressures up to 26 bar had no observable influence on lignin pyrolysis. A slight increase in phenolic yield was observed at hydrogen partial pressures up to 17 bar. However, phenolic yields tended to decrease as the pressure was increased to 26 bar. These results suggest that hydrogen may enhance hydrogenolysis, but the effects are minimal. Adding a catalyst to promote hydrogen radical production would clearly enhance demethoxylation, decarbonylation, and dehydration reactions.

CFP is being developed as a promising pathway to improve the quality of pyrolysis oils. When high-pressure hydrogen is present, the process is referred to as HYP. Zeolite catalysts, especially HZSM-5, have been frequently used in CFP based on their activity and shape selectivity toward gasoline-range aromatic hydrocarbons.[5] However, excessive coke formation and low yield of desirable hydrocarbons have limited the application of zeolites. Using catalyst promoters and hydrogen at optimized process conditions has been a strategy explored to increase the yield of desirable hydrocarbons and decrease coke formation.[54-56] Thangalazhy-Gopakumar et al.[54, 56] compared catalytic pyrolysis with HZSM-5 under helium and hydrogen on a Py-GC/MS under HYP conditions. They concluded that pressurized hydrogen or helium (up to 27.6 bar) had no influence on the yield of aromatics. Even with the presence of high-pressure hydrogen, HZSM-5 acted as a cracking catalyst only with no indication that it promoted HYD. However, the aromatic yield increased when ZSM-5 catalysts doped with Ni, Co, Mo, and Pt were used under 27.6 bar hydrogen pressure. Those metals impregnated on a ZSM-5 catalyst can activate hydrogen for HDO and HYD. Formation of a low concentration of cycloalkanes using Pt-impregnated ZSM-5 was reported in another study by Jan et al.,[55] which suggested that the noble metal dopant facilitated HDO reactions at elevated hydrogen pressure (17 bar). HYD in high-pressure hydrogen was also observed with Ni/HZSM-5 catalysts, but at atmospheric pressure, no noticeable effect on the product distribution was observed.[57] These Py-GC/MS studies suggested that catalytic pyrolysis using a pure zeolite catalyst was not affected by the presence of hydrogen. Only metal-impregnated zeolite catalysts can activate hydrogen and enhance HDO and HYD under HYP reaction conditions.

The successful work with model compounds discussed in the last section has led researchers to the conclusion that biomass CFP with atmospheric pressure reactive gas (hydrogen, in particular) is a promising pathway to produce high-quality bio-oil from biomass. This process is referred to as reactive catalytic fast pyrolysis, or RCFP. Although numerous catalysts have been tested with bio-oil model compounds, only a small subset of them have been tested with real biomass using a Py-GC/MS system. Nolte et al.[58] performed ex situ HDO of pyrolysis vapor in a tandem micro-pyrolyzer under RCFP conditions. A pure MoO_3 catalyst was found to effectively hydrodeoxygenate pyrolysis vapor to produce mostly linear alkanes and aromatics from lignin, cellulose, and corn stover. The carbon yield of larger hydrocarbons (C_{4+}) was 44 to 53% from cellulose, while the respective yields from lignin and corn stover were slightly lower at 16 to 23% and 15 to 26%. Murugappan et al.[59] performed RCFP experiments using a Py-GC/MS to evaluate supported MoO_3 (10 wt% MoO_3/TiO_2 and MoO_3/ZrO_2) catalyst performance. Both supported MoO_3 catalysts showed similar product distributions of ca. 7 C% aromatic hydrocarbons, 17 to 19 C% alkenes, 2 C% alkanes, 3 to 5 C% CO_2, 7 C% coke, and 39 C% char. In general, previous Py-GC/MS studies suggested that molybdenum-based catalysts were the most effective HDO catalysts under RCFP conditions.

5.3.2 Continuous Biomass Feed: Laboratory-Scale Reactor Studies

As discussed above, researchers have conducted a large number of model compound studies under various reaction conditions. In contrast, relatively few studies have reported real biomass in continuous laboratory reactor systems. Bubbling fluidized bed reactors are frequently used for laboratory-scale biomass pyrolysis to produce bio-oil and char for comprehensive characterization to support technology development.

Rocha et al.'s[60, 61] work on cellulose pyrolysis in a fixed bed reactor under 100 bar hydrogen atmosphere reported a higher yield of bio-oil with a slightly lower oxygen content. However, another cellulose HYP study[19] on a continuous-flow reactor in the absence of a catalyst reported varied results. Addition of 25 bar hydrogen did not have a significant effect, within experimental error, on the yields of solids, liquids, and gases from cellulose pyrolysis at 480 °C compared with an experiment at 25 bar helium. Also, the composition of the liquid product did not differ significantly in the experiments using 25 bar He or hydrogen partial pressure. However, hydrogen appeared to suppress the formation of reactive light oxygenated species like glycolaldehyde and formic acid at higher temperature (580 °C). The authors concluded that hydrogen activation was minimal without a catalyst, so little effect on biomass pyrolysis was observed.

Several groups have also demonstrated the technical feasibility of producing hydrocarbon-rich liquids at HYP conditions in continuously fed reactors using a variety of catalysts.[14, 15, 17, 18, 20, 22, 23, 62] This pathway has shown the potential to produce very low oxygen-containing intermediates (below 5 wt% dry basis) with attractive carbon yields.

Agrawal et al.[19, 20] at Purdue University reported a process that integrated non-catalytic HYP with vapor-phase catalytic HDO. A 5 wt% Pt and 2.5 wt% Mo impregnated multi-walled carbon nanotubes catalyst was found to be the optimal HDO catalyst. Carbon yield of C_{4+} hydrocarbons from wood and cellulose were 32% and 55%, respectively. However, a majority of the C_{4+} products are C_4-C_6 light hydrocarbons. Marker and co-workers at GTI integrated fast catalytic HYP with HDO (known as the IH^2 process) to produce a liquid fuel with extremely low oxygen and rich in gasoline- and diesel-range hydrocarbons.[21, 23] Different proprietary catalysts and reaction temperatures were used in the HYP and HDO reactors. At optimal reaction conditions, a C_{4+} liquid yield of 46.3 wt% from microalgae and 26.4 wt% from wood chips with less than 1 wt% oxygen content was produced from the IH^2 process. The IH^2 process consumed 39 to 61 g hydrogen/kg biomass. Theoretically, sufficient hydrogen can be produced by reforming CO and light C_1-C_3 hydrocarbon gas generated from IH^2 to maintain hydrogen balance.

RTI has also conducted HYP experiments in a fluidized bed reactor. A bio-crude yield of 23.7 wt% with oxygen content below 1 wt% was obtained at the most severe condition. Catalyst activity and stability were evaluated over a 10-day period during which biomass HYP was also performed. Catalyst activity did not appear to decrease significantly over the duration of the 10-day experiment. HDO is thought to be the dominant oxygen rejection pathway during HYP. In 20% H_2 at 20.7 bar total pressure, the hydrogen consumption measured during HYP with the commercial hydrotreating catalyst ranged from 20 to 25 g/kg of biomass fed. At higher hydrogen concentrations, the hydrogen consumption increased to 35 to 38 g/kg biomass fed.

Overall, biomass HYP can be used to produce a liquid intermediate with low oxygen content, which will lower the H_2 demand for any further downstream processing to produce a finished transportation fuel. However, feeding solid biomass into a pressurized HYP reactor remains a significant technical challenge that poses considerable risk as the technology is demonstrated at larger scale. Consequently, developing an atmospheric pressure process with similar technical performance to HYP could be an attractive alternative. Several recent studies have shown encouraging results for catalytic biomass pyrolysis in hydrogen at atmospheric pressure.

Zhang et al.[63] report results for biomass fast pyrolysis in a fluidized bed reactor with N_2 and reactive gases (H_2, CH_4, and CO). Their results showed that reactive gases affected both product yield and composition. Addition of CO and H_2 enhanced deoxygenation of pyrolysis vapor by producing CO_2 and H_2O, respectively. Consequently, pyrolysis in CO and H_2 increased the higher heating value of the bio-oil (23.7 MJ/kg and 24.4 MJ/kg, respectively) compared with bio-oil produced in a N_2 atmosphere (17.8 MJ/kg), but the bio-oil yield was lower. Lower char yield was measured for biomass pyrolysis in a CO_2 atmosphere, suggesting that char was reacting with CO_2 via the Boudouard reaction.[63]

More recently, Boateng and co-workers have conducted a series of studies on fast pyrolysis with tail-gas recycling.[64-67] The gas stream produced from biomass fast pyrolysis, consisting of primarily CO, CO_2, H_2, and light hydrocarbons, was used as a fluidizing gas and reaction atmosphere for the tail-gas reactive pyrolysis (TGRP). Significant deoxygenation was measured, and the TGRP bio-oil had a higher hydrocarbon content compared with pyrolysis in N_2. However, the TGRP bio-oil is highly aromatic and hydrogen deficient. The oxygen content of the bio-oil was reduced with a concurrent decrease of hydrogen content, suggesting that dehydration and aromatization occurred instead of HYD.

Mante et al.[7] also explored the influence of hydrogen on the pyrolysis process with a fluid catalytic cracking (FCC) catalysts. Even with the presence of 5 vol% hydrogen, bio-oil yield and its properties were improved significantly. Compared with CFP in nitrogen, RCFP with a minimal amount of hydrogen produced bio-oil with a higher heating value and pH and a lower viscosity and density. Other gases, including CO, CO_2, and tail gas from the pyrolysis process, were also found to be beneficial for obtaining a higher yield of bio-oil with improved quality.

Murugappan et al.[59] performed RCFP experiments in a horizontal quartz tube reactor using two types of supported MoO_3 (10 wt% MoO_3/TiO_2 and MoO_3/ZrO_2) and bulk MoO_3. Their study showed that the supported MoO_3 catalysts are active over a longer operating time than bulk MoO_3, which is in agreement with the study using bio-oil model compounds.[68] All of the catalysts became less effective for HDO as biomass feeding increased, suggesting rapid catalyst deactivation. Regeneration of catalysts is suggested for long-term operation of the RCFP process.

Zhou et al.[69] studied ex situ RCFP of lignin and beech wood using MoO_3 catalysts in atmospheric pressure hydrogen. RCFP bio-crude was collected in a series of condensers. Temperatures over 400 °C were required to obtain a bio-crude with 24.8 wt% oxygen content; however, the organic liquid yield was only 4.6 wt%. This low yield suggests over-cracking of the pyrolysis vapors at the ex situ RCFP conditions. In contrast, the yield of organic liquid from lignin RCFP at 450 °C catalyst temperature and 89 vol% hydrogen concentration was 16.2 wt% with 11.5 wt% oxygen content.

RTI has also explored RCFP with proprietary catalysts in a fluidized bed reactor. Biomass is continuously fed at a rate of 1 g/min into a nominal 2.54-cm diameter bubbling fluidized bed reactor maintained at a temperature between 400 and 600 °C. The multiphase product stream passes through a cyclone separator to remove solids (char and catalyst fines) and then through a condensation system that includes a shell-in-tube heater exchanger, cooled impingers, and an electrostatic precipitator. Process gas is monitored continuously with online gas chromatography, and all solid and liquid samples are analyzed to determine elemental (C, H, N, O, S) and chemical (GC/MS) composition. A detailed description of the reactor system can be found in the literature.[70, 71]

A range of different process conditions (temperature, residence time, and hydrogen concentration) was studied with a number of commercially available and developing catalysts. Table 5.2 shows the mass balances and carbon efficiency versus oxygen content for bio-crudes from RCFP using a platinum-doped solid acid catalyst (designated RTI-A9P) with varying H_2 concentrations. With the addition of hydrogen in the reactor gas at atmospheric pressure, coke production decreased and the carbon yield of organics increased substantially from 19.8% in nitrogen to 36.9% in 93 vol% hydrogen. Meanwhile, the oxygen content in organics was reduced from 22 wt% to 4.2 wt%. These results indicate that the presence of hydrogen enhanced HDO of pyrolysis vapor. The hydrocarbon concentration in the aqueous fraction also decreased as more hydrogen was added because deoxygenated hydrocarbons more easily phase separated into the organic fraction. At 93 vol% hydrogen, the water content of the aqueous fraction was 93% compared with 80% in the aqueous phase without added hydrogen. Better hydrocarbon separation equates to easier downstream processing and potentially easier aqueous fraction cleanup.

Table 5.2. Effect of hydrogen concentration on RCFP with RTI-A9P catalyst and loblolly pine as feedstock.

Hydrogen concentration/vol%	0%	25%	60%	93%
Temperature/°C	500	500	500	500
Mass balance (wt% of biomass)				
Gas	24.7	26.2	21.6	25.4
Solid	22.4	26.9	18.5	17.1
Aqueous	31.7	28.8	35.7	36.8
Organics	14.1	17.8	18.8	21.1
Wt% oxygen in organics	22	16.5	11.1	4.24
Carbon efficiency in organics	19.8	24.8	31.1	36.9
Carbon efficiency in aqueous	6.2	4.0	3.5	2.5

5.4 Discussion

Reactive catalytic biomass pyrolysis is a promising process for using hydrogen during in situ catalytic biomass pyrolysis to maximize the biomass carbon and energy recovery in a low oxygen content, thermally stable bio-crude intermediate that can be efficiently upgraded into a finished biofuel. The key to this novel process is developing a robust catalyst that efficiently uses hydrogen for HDO and increases the hydrogen-to-carbon ratio in volatile products to limit char and coke formation. The amount of oxygen removed during the RCFP process is the primary metric for a successful catalyst, but the use of hydrogen also increases carbon efficiency in the liquid bio-crude product. A wide array of parameters ranging from catalyst properties to process conditions can affect the observed HDO activity and coke formation rate measured in model compound screening experiments. A wide variety of catalysts have been screened for HDO activity with model compounds and with real biomass. Figure 5.2 shows the measured carbon efficiency (C_4^+ products) as a function of oxygen content measured for bio-crude intermediates produced from CFP, HYP, and RCFP. While HYP clearly demonstrates the highest yields at the lowest oxygen content, the RCFP has been successfully developed to the point where greater than 42% of the carbon input from biomass can be recovered in a bio-crude intermediate with less than 8 wt% oxygen.

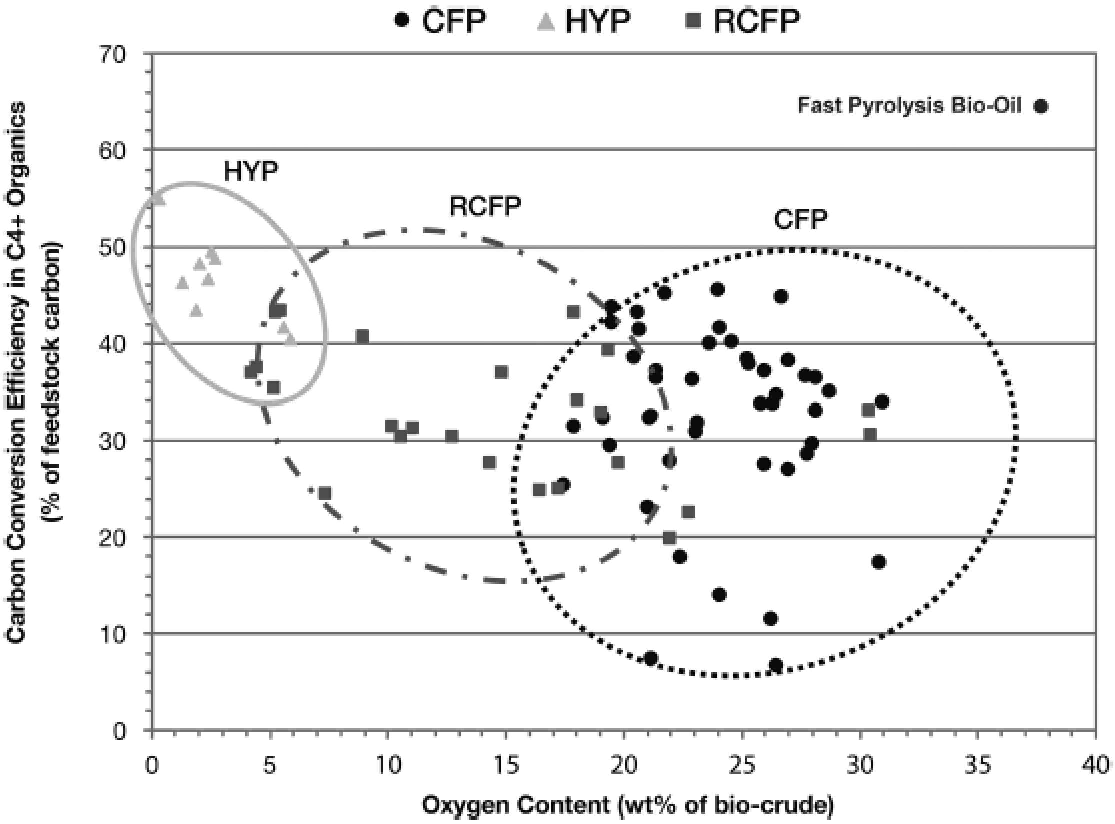

Figure 5.2 Bio-crude oxygen content as a function of carbon efficiency for CFP, RCFP, and HYP.

The commercial viability of these direct biomass liquefaction pathways can be assessed by comparing how the relative yields, hydrogen demand, and carbon recovery potential affect the preliminary techno-economics of each process. The biofuels yield and hydrogen demand are estimated from the laboratory material balances and measured bio-crude oxygen content. The calculated fuel yield (light gray bars) presented in Figure 5.3 is based on upgrading the bio-crudes produced from each process in a hydroprocessing step. The calculation assumes no carbon losses during hydroprocessing. The hydrogen demand determined for each conversion process (dark gray bars) shown in Figure 5.3 was experimentally measured, while the hydrogen demand for upgrading (medium gray bars) was calculated by assuming the remaining oxygen in the bio-crude was removed as water and the hydrogen-to-carbon ratio in the finished biofuel is two. The volumetric yield of the finished biofuels is based on a density of 0.8 g/ml, similar to diesel.

Figure 5.3 Summary of the biofuel yield and hydrogen demand for three bio-oil pathways.

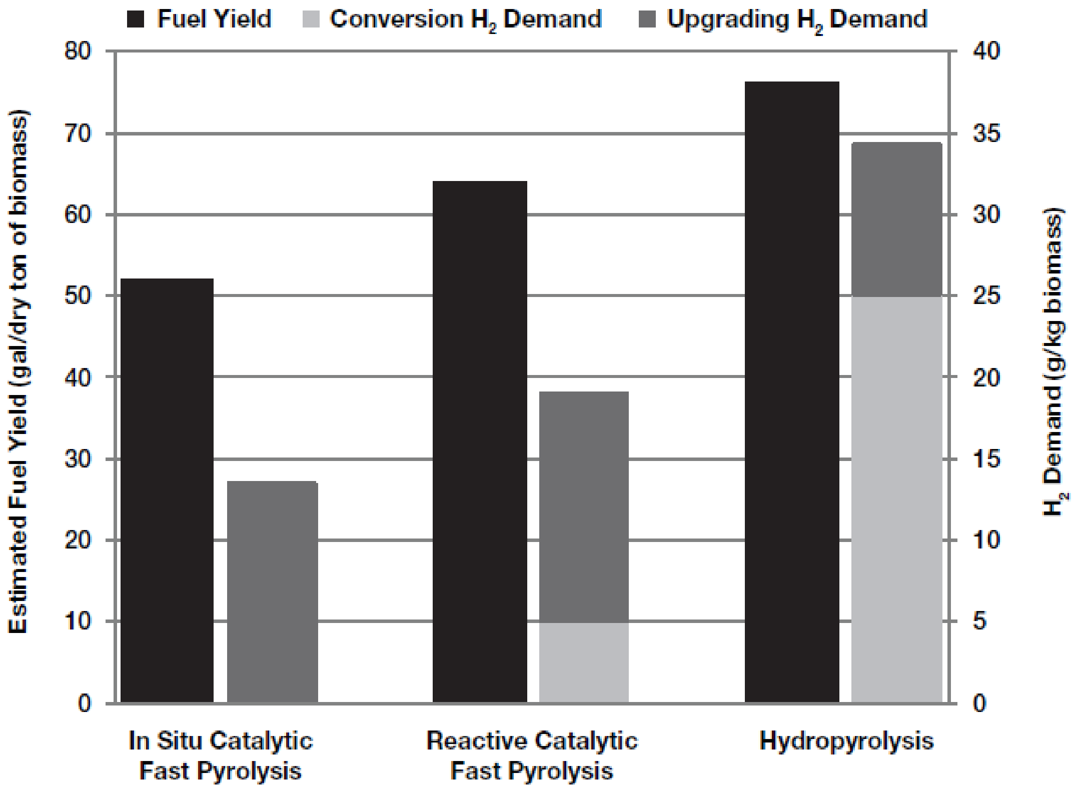

Figure 5.3 Summary of the biofuel yield and hydrogen demand for three bio-oil pathways.

The total hydrogen demand (sum of the medium and dark gray bars) for each process effectively correlates with the bio-crude yield because more hydrogen is required to deoxygenate and upgrade the intermediate bio-crude produced. The CFP and RCFP processes have about the same hydrogen demand for upgrading, but the RCFP process uses hydrogen in the conversion step, so the total hydrogen demand is higher. Less hydrogen is required for deoxygenating the HYP bio-crude because it has low oxygen content, but the hydrogen demand during HYP is comparatively high because carbon efficiency is higher and there is near complete HDO in the conversion step.

5.5 Summary and Future Work

In summary, reactive gases, especially hydrogen, have led to improved bio-oil quality by slightly reducing oxygen content even in the absence of catalysts. Although free radical mechanisms are proposed, researchers generally do not have an in-depth understanding of how the chemistry of biomass fast pyrolysis changes by adding reactive gases. The resulting bio-oil from noncatalytic pyrolysis with reactive gases is highly aromatic and hydrogen deficient. Catalysts to prompt the HYD reaction are recommended to add to the reaction network to further improve the quality of the bio-oil.

Many of these studies have been conducted with model compounds or in small laboratory reactors with biomass. The technology is promising but requires scale-up and demonstration to become a commercial reality. One key activity for technology development includes testing the RCFP concept in pilot-scale reactors with continuous biomass feeding and integrated reaction/regeneration to optimize the process and evaluate the long-term performance of catalysts. Pilot-scale testing will require parallel development and scale-up of catalysts with suitable HDO activity and physical strength to maximize performance and minimize catalyst loss by attrition. Removing coke deposits during regeneration will be required to maintain catalyst activity, but irreversible deactivation by sintering or catalyst poisoning will require substantial investigation to guarantee long-term performance.

Upgrading RCFP bio-crude into refinery blendstock or finished biofuel will require additional research and development. To date, large enough reactor systems to produce enough bio-crude for upgrading studies have not been available. A working hypothesis assumes that RCFP bio-crude will be easier to hydroprocess than CFP or fast pyrolysis intermediates. The true test of the RCFP process will be to evaluate the final biofuel yield and hydrogen and compare it to existing advanced biofuels processes.

A clear logistical and economic challenge for this technology is the need for hydrogen in the pyrolysis reactor. Co-locating future plants with a source of hydrogen, like a petroleum refinery, methanol synthesis process, or integrated gasification combined-cycle plant, could be an option to meet the hydrogen demand of the RCFP process. Another option is to leverage the development of small-scale hydrogen production processes that are being developed as a strategy for hydrogen fueling stations of the future. Regardless, integrated process concepts that minimize capital costs to maximize the economic feasibility of the RCFP process will need to be developed, demonstrated, and deployed.

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