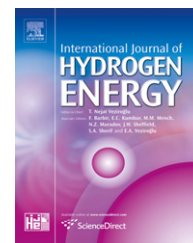


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Production of synthesis gas by partial oxidation and steam reforming of biomass pyrolysis oils

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ABSTRACT

As the lowest cost biomass-derived liquids, pyrolysis oils (also called bio-oils) represent a promising vector for biomass to fuels conversion. However, bio-oils require upgrading to interface with existing infrastructure. A potential pathway for producing fuels from pyrolysis oils proceeds through gasification, the conversion to synthesis gas. In this work, the conversion of bio-oils to syngas via catalytic partial oxidation over Rh–Ce is evaluated using two reactor configurations. In one instance, pyrolysis oils are oxidized in excess steam in a freeboard and passed over the catalyst in a second zone. In the second instance, bio-oils are introduced directly to the catalyst. Coke formation is avoided in both configurations due to rapid oxidation. H₂ and CO can be produced autothermally over Rh–Ce catalysts with milli-second contact times. Co-processing of bio-oil with methane or methanol improved the reactor operation stability.

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1. Introduction

Concerns about energy independence, carbon tax, global warming, and peak oil all indicate a need to find alternatives to petroleum to satisfy our fuel needs. However, the benefits derived from a hundred years of infrastructural investment are not the only reasons to consider alternatives that look very much like petroleum. Carbon-based fuels have exceptionally high energy density. As liquid fuels, they are easily stored and transferred from the refinery to the pump to the automobile. They are familiar, and an entire fleet of vehicles in every country in the world already makes use of them. Liquid carbon-based fuels are an entrenched technology and will not be easily replaced. In addition, alternatives put forward for automotive transportation often involve liquid carbon fuels: fuel cell cars can store hydrogen via liquid fuels, making use of

an on-board reformer [1–4]. Electric cars by themselves require long charging times, and as such, hybrid electrics appear to offer the best of both worlds.

For these reasons, an alternative source of carbon-based fuels is required. Biomass represents the only source of renewable fixed carbon. Estimates indicate that the US has enough biomass to offset up to 30% of its petroleum consumption through the use of biomass [5].

However, converting biomass to liquid fuels is not trivial. Biomass is a distributed resource: it is land intensive, has high oxygen and water content, and low energy density. Whereas petroleum refining benefits from an economy of scale because high energy petroleum can be shipped and pumped, the low density of hay bales and wood chips require some form of local densification before they can be upgraded on a large scale. For this reason, current biomass models are associated with

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smaller village-sized refineries local to the biomass resource, such as ethanol plants. To reduce the costs of second-generation biofuels, alternative technologies are required that will allow biomass to benefit from economies of scale.

One such method of biomass densification is fast pyrolysis, which benefits from years of research and is an industrially demonstrated technology [6,7]. By rapidly heating biomass in the absence of oxygen, pyrolysis oils (bio-oils) can be formed. These liquids have higher energy density than biomass: they are still oxygenated and contain water, but they can be pumped or shipped more efficiently to be upgraded at a central facility, thereby benefiting from economy of scale [8–10]. In addition, pyrolysis represents a chemical step that can be combined with ash removal: at less than 0.1%, bio-oils contain much less ash than their original biomass source, the ash being removed with the solids (char), a by-product of pyrolysis [11]. Bio-oils vary greatly by feedstock and method of preparation and, as such, require further upgrading to convert them to usable fuels compatible with existing infrastructure.

Several options can be considered for further upgrading pyrolysis oils to high-quality liquid fuels. Perhaps the most versatile pathway for producing fuels from pyrolysis oils proceeds through gasification, the conversion to synthesis gas (syngas). Syngas, a mixture of H_2 and CO, can then be converted to fuel alkanes or alcohols, eg. by the Fischer Tropsch synthesis, or it can be converted to a carbon neutral H_2 source for use in other refining steps or the production of ammonia. As such, the two-step process of local pyrolysis and either local or large-scale gasification provide a novel carbon and hydrogen vector for use in refining and the production of second-generation biofuels.

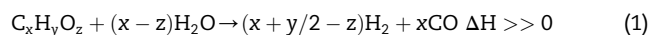
1.1. Catalytic gasification

Low ash pyrolysis oils can be converted to syngas by catalytic steam reforming. Nickel is the typical catalyst of choice for the steam reforming of several bio-oil model compounds and pyrolysis oil constituents [7,12–14]. In addition, whole bio-oils or the aqueous phase of bio-oils have been steam reformed over Ni in various reactor configurations [7,15–19]. However, the reforming of pyrolysis oils presents significant challenges, most of which have to do with coke formation due to the dehydration and polymerization of pyrolysis liquids. Whole bio-oils are subject to even greater coke formation due to the polymerization of aromatic and unsaturated components in the lignin-derived fraction.

Several strategies have been implemented to solve the coke problem, including catalyst choice, steam addition, fuel blending, and periodic reactivation via steam or burn off.

Noble metals have been investigated for the steam reforming of pyrolysis liquids [20–22]. Pt and Rh especially show greater stability and resistance to coking than cheaper alternatives. Another alternative is to not use a catalyst at all: van Rossum reports efficient gasification of pyrolysis liquid which can then be cleaned in a second stage involving a catalyst [19,23].

Coke formation can also be mitigated by using a greater quantity of steam in the process (higher steam-to-carbon ratio (S/C)). In such a case, the production of H_2 increases, but so do heat loads, both to create steam and as steam reforming is endothermic (Equation (1)).

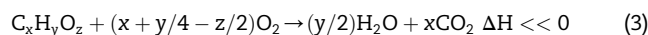
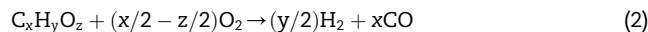


Reforming experiments reported in the literature are typically carried out using excess steam with $6 < S/C < 12$, and no examples of steady catalytic reactor operation are reported for $S/C < 3$.

Blending of pyrolysis oils can also alleviate coke formation. Mixing bio-oils with methanol enhances their stability [24,25]. Czernik et al. investigated the steam reforming of aqueous phase bio-oil over a fluidized bed of Ni catalysts with the addition of natural gas [15]. Their reactor demonstrated fuel flexibility, and the addition of natural gas promoted catalyst stability and longevity.

Solid carbon can also be eliminated by burn off. Domine et al. demonstrated the efficacy of pyrolyzing bio-oil for H_2 production over noble metal catalysts, and periodically reactivated by reacting coke with oxygen [26,27]. Oxidation can occur in the presence of steam reforming, and can increase the conversion in a non-catalytic system [10]. However, the presence of O_2 reduces both the experimental [18,19,21] and theoretical [28] yield of H_2 .

If a sufficient amount of O_2 is present, partial oxidation can occur autothermally, with oxidative chemistry alleviating the heat load for the reactor according to Equations (2 and 3). Autothermal reforming of bio-oil is desirable because the heat of reaction drives the chemistry, and reactors can be scaled more easily. Stable autothermal reforming to H_2 would even allow bio-oil to be used as a liquid fuel for automotive fuel cell applications.



Depending on the x:z ratio, Equation (2) can be weakly exothermic or endothermic. Some complete oxidation, Equation (3), provides enough energy to operate partial oxidation autothermally. Biomass and bio-oil model compounds have been converted to syngas via catalytic partial oxidation (CPO) over noble metal compounds [29–31]. Additional advantages of CPO include the availability of O_2 for the removal of coke, high heat transfer rates and thermal efficiency, millisecond contact times, high conversion, and equilibrium syngas production.

This work represents a comprehensive exploration of catalytic gasification of pyrolysis liquids. Several reactor configurations are detailed, and numerous experiments on a variety of pyrolysis oils are considered, including the CPO of pyrolysis oils, staged non-catalytic partial oxidation-catalytic steam reforming, and catalytic oxidative reforming over noble metals.

2. Material and methods

2.1. Feedstock

Bio-oils were prepared at NREL by fast pyrolysis of three feedstocks using different reactor configurations. Poplar wood was pyrolyzed in a vortex reactor at gas temperature of 455 °C [32]. The unit included a hot gas filter for char separation from

pyrolysis vapors. Pine was processed in a bubbling fluidized bed reactor operating at 500 °C with 2 s vapor residence time. An entrained flow tubular reactor was used to produce bio-oil from mixed hardwood. The latter two units were provided with cyclones for the gas/char separation. The elemental and moisture composition (TitroLine Karl–Fisher) of the bio-oils are shown in Table 1. In addition to many oxygenated organic compounds, bio-oils include a significant amount of water. Over time the properties of bio-oils change and some phase separation can occur due to polymerization and dehydration [33,34]. In this study, bio-oils were reconstituted using vigorous mixing and 10–50 wt% methanol addition [35]. Although it may not be necessary or desirable in large scale application, addition of methanol stabilizes bio-oil, reduces viscosity, and facilitates atomization, all considerable benefits in lab scale setups for which bio-oils may be stored between production and use. Phase separation persisted in the pine bio-oil; the lighter fraction was used for Direct Catalytic Partial Oxidation experiment and is reported in Table 1.

2.2. Catalyst preparation

All catalysts were prepared using incipient wetness impregnation. α -Alumina foam monoliths of 20 pores per linear inch (ppi), 45 ppi, and 80 ppi were obtained from Vesuvius Ceramics. The foams were drop coated with aqueous slurry of γ -alumina powder (1 wt% of the original monolith), dried, and calcined in a furnace at 600 °C for 6 h. The foams were then coated with an aqueous solution of $\text{Rh}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 1 wt% each of Ce and Rh. After drying, catalysts were calcined at 600 °C for 6 h.

Spheres were made in a similar fashion: 1.3 mm diameter α -alumina spheres (Saint Gobain Norpro) were coated with aqueous 1 wt% $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution dried, and calcined at 600 °C for 6 h to form a ceria washcoat. The spheres were then coated with 1 wt% each Rh and Ce in the same method as the foams.

2.3. Experimental systems

The two main reactor configurations employed included direct catalytic partial oxidation (DCPO) and staged freeboard gasification followed by catalytic reforming. The direct catalytic partial oxidation route offers shorter contact times and higher rates of heat transfer; the staged gasification/steam reforming route provides greater protection to the catalyst

from inorganic materials in the feed and increases yield of hydrogen due to water-gas shift (WGS).

2.3.1. Direct catalytic partial oxidation (DCPO)

Liquid fuels were fed by a fixed volume syringe pump at a rate of 35–70 g/h. In experiments with methanol addition, pyrolysis oil and methanol were premixed (eg. in a 50–50 wt% solution). In each reactor scheme of the DCPO experiments, liquid fuel was introduced using a stainless steel nebulizer, which employs a gas pressure drop to break liquid droplets into a fine mist. Flow rates of bio-oil are given in methane equivalent volumetric gas hourly space velocity (GHSV), which is defined as the volumetric gas flow that would be observed if all carbon in the feed was in the form of CH_4 per unit volume of catalyst. N_2 and O_2 flows were controlled using mass flow controllers (Brooks 5850i). The fuel/air spray flowed into a 19mm internal diameter (ID) quartz tube over a 3 cm bed (6.4 g) of alumina foam monoliths coated with approximately 0.06 g each of Rh and Ce. In some experiments CH_4 was added to the gas mix either through a nebulizer or directly into the reactor.

The fuel nebulizer was clad in a 5/16" tube allowing water flow in the jacket to maintain low temperatures within the nebulizer necessary to prevent upstream heating of the bio-oil. Water, when added to the reactor, was fed through a second nebulizer parallel to the first. The reactor vessel was sealed with a Teflon block and an O-ring. In some experiments, heat was supplied externally using heat tape or a furnace around the reactor tube. In these configurations, a thermocouple was inserted upstream of the catalyst or on the reactor wall to quantify the preheat temperature. A typical reactor setup is depicted in Fig. 1.

Temperatures were monitored at the back face of the catalyst bed in all experiments. The reactor effluent passed through a condenser; gases were sampled by syringe and analyzed by gas chromatography (GC). An HP 5890 GC equipped with a thermal conductivity detector was calibrated for H_2 , N_2 , O_2 , CH_4 , CO , CO_2 , C_2H_2 , C_2H_4 , and C_2H_6 (N_2 was used as an internal standard). A variety of experiments were conducted exploring the effects of catalyst pore size, air delivery, steam addition, the proximity of the nebulizers to the catalyst, and external heating. In all experiments reported, O_2 conversion was 100%.

2.3.2. Staged partial oxidation (POX) – steam reforming (SR)

Staged partial oxidation/steam reforming of bio-oil was carried out in a bench-scale system shown in Fig. 2. Poplar bio-oil diluted with 10 wt% methanol was fed at 60 g/h using a membrane pump to the top of the 32 mm ID, 45 cm long tubular quartz reactor, which contained in the bottom section a fixed bed comprised of 18 g of catalyst (1 wt% Rh, 1 wt% Ce on alumina) mixed with 70 g of α -alumina. In the top section (freeboard), the liquid in the form of a very fine mist produced by a 120 KHz ultrasonic nozzle (Sono-Tek) contacted with air (POX tests) or with air and steam (POX/SR experiments). $\text{GHSV} = 30,000 \text{ h}^{-1}$ (compared to $2,000 \text{ h}^{-1}$ used for industrial steam-methane reforming). Process performances were determined at varied temperature, carbon-to-oxygen (C/O, where O is counted only from air, ie. neglects fuel and water O) and steam-to-carbon (S/C) molar ratios (S/C does not count the latent water contained in bio-oil). Another description for

Table 1 – Elemental and moisture content of bio-oils.

	Poplar	Pine ^a	Hardwood
C, wt%	48.1	21.8	45.0
H, wt%	7.2	7.8	6.9
O, wt%	44.7	70.4	48.1
H ₂ O, wt%	17	51	29

a Pine bio-oil separated in two fractions; the lighter top fraction was used.

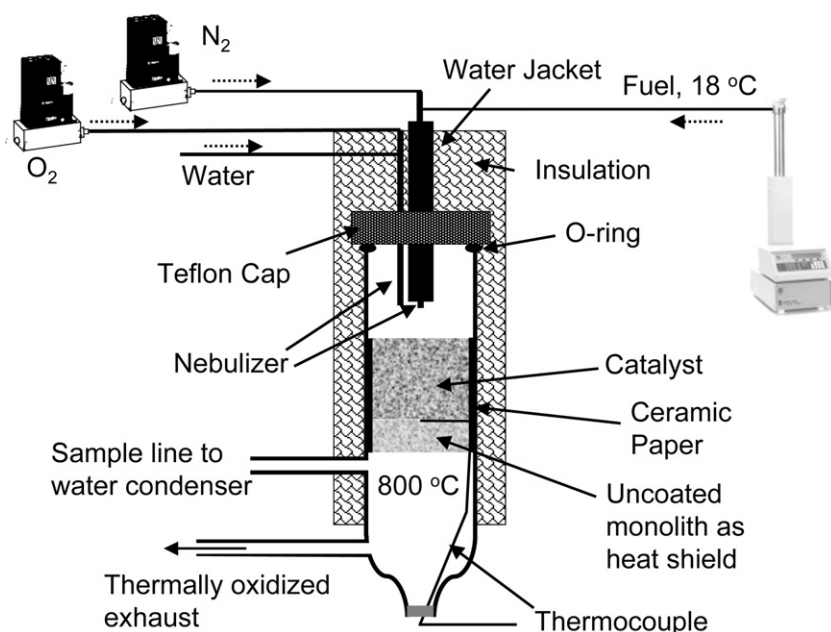


Fig. 1 – DCPO reactor system.

oxidation amount is λ , the ratio of air added to that required for complete oxidation.

Partial oxidation occurred mostly in the freeboard (residence time $T = 0.88$ s), while steam reforming (SR) and WGS occur on the catalyst ($T = 0.12$ s). The reactor was maintained at temperature 700 °C–800 °C by an electrically-heated furnace. The steam excess and some organics were

collected in two condensers. The outlet gas flow rate was measured by a dry test meter. The concentrations of CO_2 , CO , and CH_4 in the product gas were monitored by an infra-red analyzer (NDIR Model 300 from California Analytical Instruments); the H_2 concentration was tracked by a thermal conductivity monitor TCM4. In addition, the gas was analyzed every 4 min by an on-line Varian micro GC, which provided

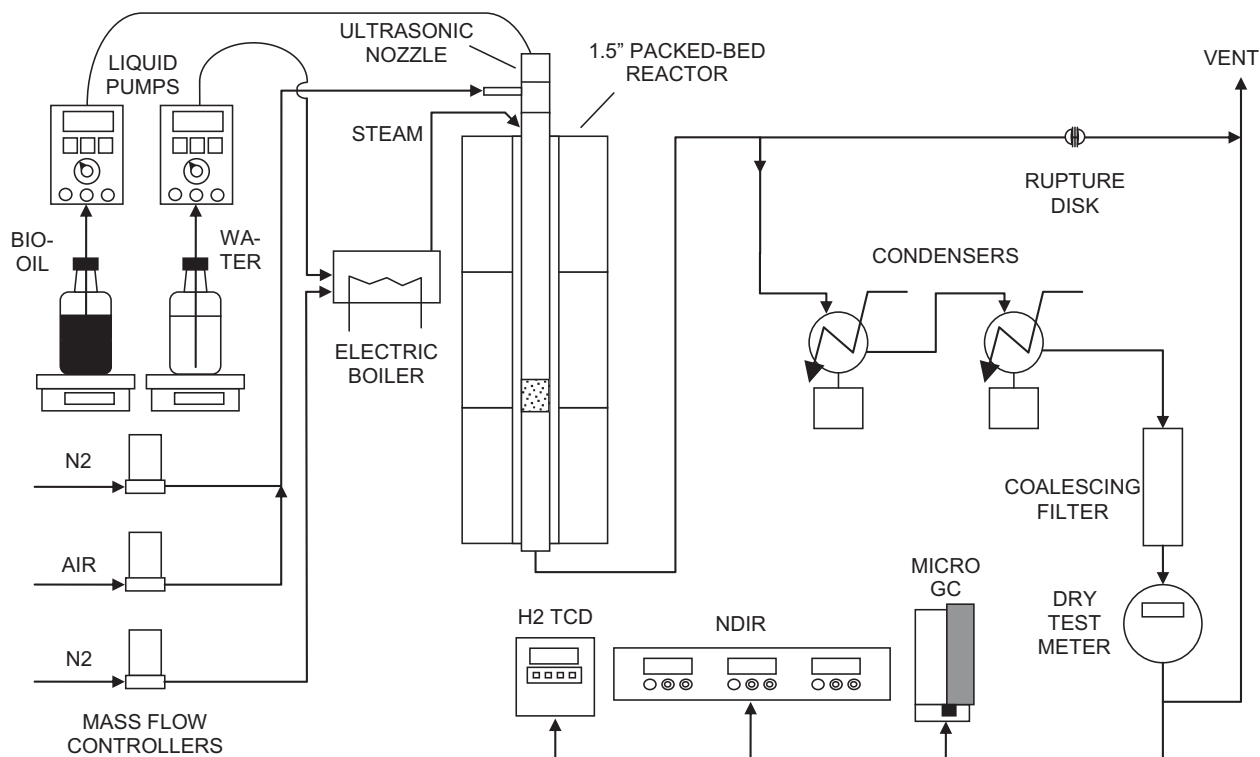


Fig. 2 – Schematic of the bench-scale POX/steam reforming system.

concentrations of H_2 , CO , CO_2 , CH_4 , C_2H_4 , O_2 , and N_2 . The temperatures in the system, as well as the flows, were recorded and controlled by the OPTO data acquisition and control system.

3. Results

3.1. Direct catalytic partial oxidation system (DCPO)

The partial oxidation of pure pine pyrolysis oil in the presence and absence of water was studied in the DCPO system (Fig. 1). N_2 flowed through a water cooled fuel nebulizer, positioned 1 mm above the catalyst bed comprising a 20 ppi/45 ppi/45 ppi catalysts on top of a 45 ppi uncoated foam acting as a heat shield. O_2 flowed through a second stainless steel port also positioned 1 mm above the catalyst. Fig. 3 shows gas product yields obtained by the partial oxidation of pine bio-oil with no water addition as a function of C/O, which corresponds to an atomic ratio of carbon in bio-oil to the added oxygen. Yields are defined as conversion of atomic C or H atoms in the fuel to a given product, such as total C in fuel converted to CO , total H in fuel converted to H_2 . With these definitions, 100% yield of CO represents all carbon exiting in the form of CO ; 100% yield of H_2 represents all H in the fuel (including that in water from bio-oil) converted to H_2 . Note that with water addition ($S/C > 0$), yield of H_2 can exceed 100% because of the steam contribution via SR and WGS.

At GHSV $\sim 14000 \text{ h}^{-1}$ and residence time $\tau \sim 65 \text{ ms}$, the average conversion of bio-oil carbon to CO and CO_2 was approximately 97%. The maximum in syngas production was observed at $C/O = 0.71$; as O_2 increases (lower C/O), oxidation of syngas product results in an increase in water and CO_2 , consuming valuable syngas. At higher C/O, a buildup of coke impairs the reactor operation, resulting in an inefficient conversion.

In comparison, Fig. 4 depicts the same experiment with the addition of water ($S/C = 6.3$). Fuel (0.024 mol/min) and N_2 flowed through a nebulizer positioned 1 cm above the catalyst bed comprising 45 ppi/45 ppi/80 ppi catalyst atop a 45 ppi ceramic

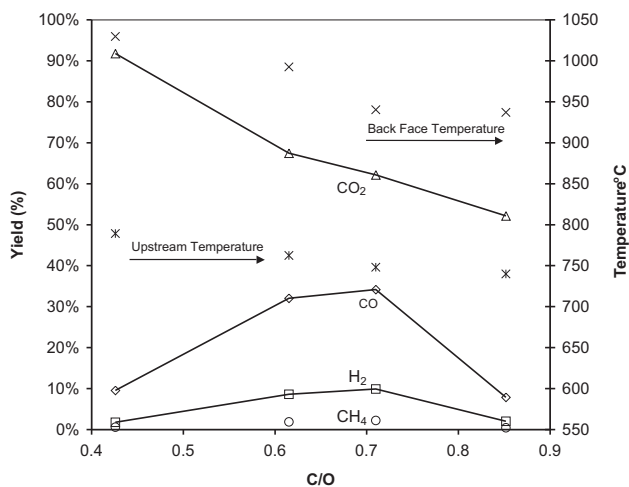


Fig. 3 – Catalytic partial oxidation of pine pyrolysis oil in a furnace.

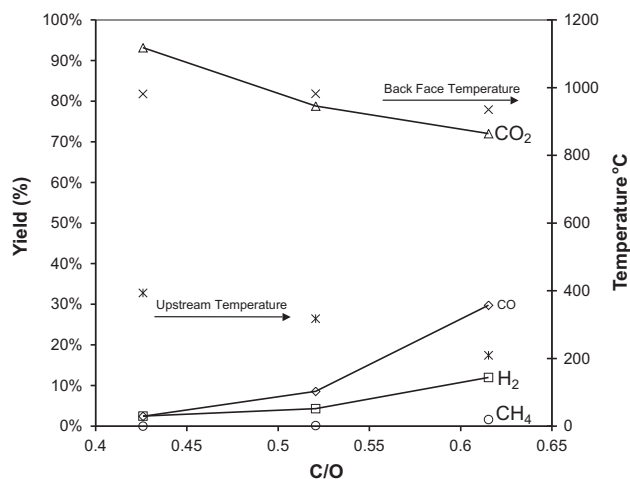


Fig. 4 – Catalytic partial oxidation of pine pyrolysis oil in a furnace, $S/C = 6.3$.

monolith acting as a heat shield. Water (0.072 mol/min) and O_2 flowed through a second nebulizer also positioned 1 cm above the catalyst bed. At GHSV $\sim 34000 \text{ h}^{-1}$ and $\tau \sim 26 \text{ ms}$, the average carbon conversion was $\sim 96\%$. The addition of water had little effect on the product stream in this configuration: yields of CO and H_2 were comparable for $C/O = 0.63$ in both experiments. However, water addition increases the yield of syngas with an increase in C/O: SR becomes more competitive with limited oxidation.

Water acted as a significant heat sink, likely decreasing upstream temperatures and hindering reaction rates, though these effects are compensated by an increase in H_2 and CO due to SR. Upstream temperatures were significantly lower with the addition of H_2O due to the heat loss to vaporization and the heat capacity of steam. Back face temperatures were similar with and without water addition, consistent with similar product spectra. This suggests that under these operating conditions, SR was not sufficiently fast to significantly affect the product spectrum.

The effect of increasing O_2 is apparent as C/O decreases: yield of syngas decreases while CO_2 increases. In both experiments, each data point represents the average of three runs at the given C/O ratio (defined as C in fuel to O co-fed in air), with the exception of $C/O = 0.85$, which represents one data point.

Oxidation is efficient at maintaining a coke-free reactor; however, high O_2 addition consumes syngas product resulting in a decrease of syngas yield for $C/O < 0.6$. On the other hand, limited availability of oxidative chemistry results in coke deposition thus compromising syngas selectivity; consequently, the syngas yield decreased for $C/O > 0.7$.

An 80–20 wt% hardwood pyrolysis oil/methanol solution was converted to syngas using the same reactor system (Fig. 1). To reduce coke deposition in the zone between fuel introduction and the catalyst, a water cooled nebulizer was positioned 1 mm above the catalyst bed, which comprised 20 ppi/45 ppi/45 ppi catalysts atop a 45 ppi uncoated heat shield. N_2 was used as a carrier gas in the nebulizer; O_2 entered through a separate stainless steel tube positioned 0.2 mm above the catalyst bed. The product yield data are depicted in

Fig. 5. The first three points explore $C/O = 0.9$, after which the air flow rate was adjusted to raise the C/O to 1.1. Under these conditions, H_2 and CO yields were relatively constant, at $\sim 25\%$, and at 65% respectively. There is not an obvious change in syngas production with this small change in C/O , though the higher C/O shows some signs of possible deactivation (decreases in CO , H_2) whereas the lower C/O showed a relatively constant or perhaps even increasing yield of syngas.

At $GHSV \sim 18000 \text{ h}^{-1}$ and $\tau \sim 47 \text{ ms}$, the overall carbon-to-gas conversion was $\sim 90\%$. Although the reactor ran smoothly for the entire experiment, coke buildup was noticeable in the reactor upon shutdown.

A series of experiments were performed to explore the possibility of autothermal laboratory-scale operation. The reactor was heated to 300°C and lit off with CH_4 for 5 min to allow the catalyst to achieve reaction temperature. Then the flows of N_2 , O_2 , methane, and pyrolysis oil mixture were adjusted to the desired levels at time = 0 min. A poplar-methanol solution was converted to syngas autothermally. The feed system was not water-cooled, and the air blown nebulizer was positioned 2 cm above the catalyst bed.

Data for this experiment are depicted in Fig. 6. At $GHSV \sim 35000 \text{ h}^{-1}$ and $\tau \sim 30 \text{ ms}$, the initial conversion is 85% . Although at 50 min, C/O was changed from 1.2 to 0.85, the temperature in the reactor decreased and so did the yield of syngas with a notable increase in the production of methane.

Although the reactor achieved autothermal operation for some time, coke deposition upstream of the catalyst and within the fuel feed system precluded a long-term steady-state operation and the reactor shut down after approximately 200 min on stream. Trends in CO_2 , H_2 , and CH_4 were consistent with a steady loss of activity, likely due to coke deposition in the reactor.

In order to improve autothermal operation, a poplar pyrolysis oil/methanol solution was partially oxidized with the addition of methane and air. Flow rates for bio-oil, CH_3OH , and CH_4 were respectively 0.012, 0.009, and 0.004 mol C/min. The overall air/fuel stoichiometry corresponded to $C/O = 0.97$. Liquid fuels were propelled by air through a nebulizer

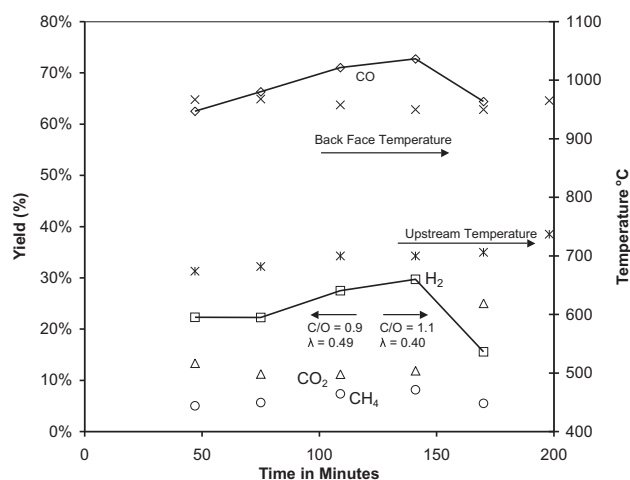


Fig. 5 – Catalytic partial oxidation of 80 wt% hardwood bio-oil, 20 wt% methanol (83–17 mol%) in a reactor preheated to 700°C .

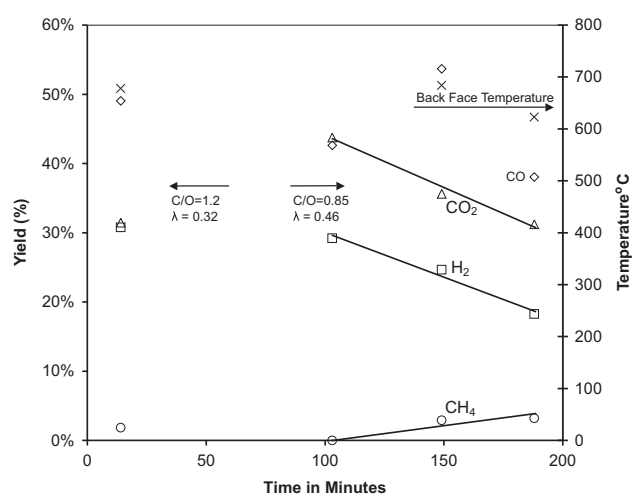


Fig. 6 – Autothermal CPO of a 50–50 wt% poplar bio-oil/methanol solution.

positioned 5 mm above the catalytic bed, comprising three 80 ppi foam monoliths loaded with noble metals and one uncoated foam monolith acting as a heat shield at the back face. Results are depicted in Fig. 7.

The addition of CH_4 significantly improved the autothermal process and allowed for over 3 h of steady state operation. At $GHSV \sim 22000 \text{ h}^{-1}$, $\tau \sim 54 \text{ ms}$, and $C/O = 0.97$, the total carbon-to-gas conversion was $\sim 96\%$ (counting CH_4 as product), though significant amounts of CH_4 were observed. A similar effect of CH_4 addition was also observed for the DCPO of pine bio-oil; the reactor operated autothermally until it was shut down when all fuel was consumed. Fig. 8 shows the dry product gas composition (on an N_2 -free basis).

The 21 mol% methane addition represented the best combination of steady activity and minimal co-feed for pine pyrolysis oil reforming. Experiments carried out with 15 mol% methane ceased operating autothermally after 1 h while those

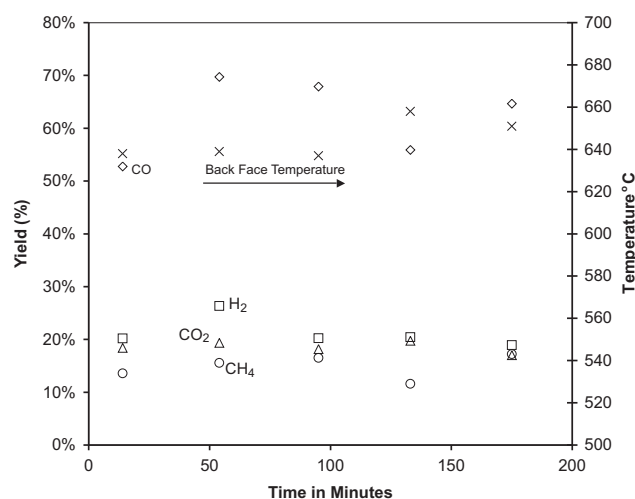


Fig. 7 – Autothermal partial oxidation of a 45–45 wt% poplar oil-methanol solution with 10 wt% CH_4 addition. $C/O = 0.97$, $\lambda = 0.37$.

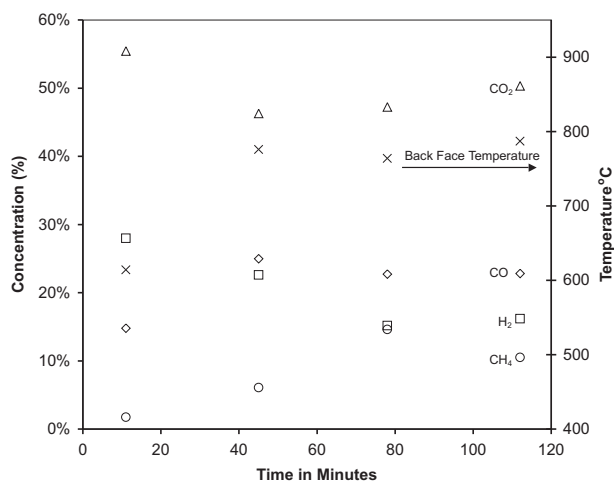


Fig. 8 – Dry effluent concentrations from the catalytic partial oxidation of pine oil with 21 mol% CH₄, 79% pyrolysis liquid by carbon content, at C/O = 0.47, λ = 0.84.

with 25 mol% methane did not show a greater benefit in product stability than during the experiment depicted in Fig. 8. It is worth noting that in almost all of these experiments, the CH₄ effluent was approximately equal to inflow.

3.2. Staged partial oxidation

Staged thermal/catalytic partial oxidation tests of bio-oil were conducted using the system presented in Fig. 2. The feedstock was a 90/10 wt% poplar bio-oil/methanol solution. Fig. 9 shows the product gas composition at different POX process conditions (top) and the corresponding H₂ and CO yields (bottom).

At GHSV 10,000–11,000 h⁻¹, bio-oil to gas conversion for thermal/catalytic POX approached 85%. Though some carbon deposits formed and slowly deactivated the catalyst, regeneration by air oxidation restored its full activity. As expected, H₂ and CO yields were greater at higher temperature and lower C/O ratio; they decreased to less than 40% at C/O of 0.77 as shown in Fig. 10. The opposite trend was observed for CO₂. Small amounts of carbon were converted to CH₄ and C₂H₄ (traces).

3.3. Staged partial oxidation/steam reforming

When staged partial oxidation of bio-oil was carried out in the presence of steam, the product gas composition significantly changed. Fig. 10 shows the gas composition produced from the process carried out at 750 °C, C/O of 1.16, S/C = 1.6, GHSV = 11,000 h⁻¹, τ = 0.12 s.

During the 5 h test, the catalyst performance exhibited by the production of H₂ remained almost constant, though some carbon deposit in the reactor (<2 wt% of carbon fed) was observed. However, CH₄ concentration in the product gas increased, suggesting catalyst deactivation. The carbon-to-gas conversion was 91% and the hydrogen yield was 7.2 g per 100 g bio-oil. This yield would increase to 9.3 g/100 g bio-oil with complete WGS. After that test, the catalyst was regenerated by air oxidation and reused for other tests carried out under the

same process conditions. In the second test, the performance was almost equal to that from the first experiment (WGS conversion slightly decreased with every regeneration cycle).

3.4. Thermodynamic calculations

A thermodynamic analysis was performed using the Chemkin 4.1.1 software package. Bio-oils were simulated using a combination of phenol, methanol, formic acid, formaldehyde, and water. Isothermal equilibrium was determined by holding pressure constant and utilizing the measured catalyst back-face temperatures. Besides reactants (also including O₂ and CH₄) and N₂, equilibrium products allowed were CO, CO₂, C₂H₂, C₂H₄, and C₂H₆. Selected experimental results are presented in Table 2 along with thermodynamically predicted product concentrations and yields. Concentrations are reported on dry, N₂-free gas basis. The differences between experimental gas composition and yields and those calculated are probably due to catalyst deactivation, bio-oil decomposition, and process kinetics (short residence time): about 35% of bio-oil comprises oligomeric lignin-derived compounds of an average molecular weight of 800 that react more slowly and have a tendency to carbonize [36].

4. Discussion

Pyrolysis oils from three different sources were converted to syngas in millisecond contact times. While varying process conditions and bio-oil quality affect the process stability, the addition of co-feeds such as CH₃OH or CH₄ can improve operation. Autothermal reforming of pyrolysis oils is also possible and is more stable with the addition of CH₄. With the incorporation of a WGS stage, CO can be consumed and H₂ produced, thereby increasing H₂ production.

The addition of CH₄ to DCPO experiments renders the catalyst more stable. However, CH₄ is barely consumed in these experiments. That is to say, although no labeling of particular methane molecules was performed, the addition of CH₄ to the reactants increases its content in the effluent by nearly as much. Methane is much more stable than most of the constituents in pyrolysis oils: activation on a noble metal catalyst requires the breaking of the C–H bond for methane [37], whereas oxygenated molecules typically adsorb via electron rich oxygen atoms [38]. Methane is less reactive than bio-oil over noble metals. However, as a gas, CH₄ mixes well with air flowing from the nebulizer.

Pyrolysis aerosols, on the other hand, must evaporate or react on the catalytic surface in the form of a liquid droplet, and the short distance allowed for mixing renders it highly non-ideal. Thus, the transport of bio-oil to the catalyst surface is inferior to that of CH₄. In addition, cold bio-oil droplets can reduce the surface temperature of the catalyst prior to oxidation, which may inhibit reaction rates. The net effect is that co-fed methane allows for more of the catalyst to stay at steady reaction temperatures, even while only a fraction of the CH₄ is consumed. Where bio-oil is not reaching the catalyst, the addition of CH₄ allows the catalyst to be hot and active; where bio-oil is reaching the catalyst, CH₄ merely passes through like a diluent.

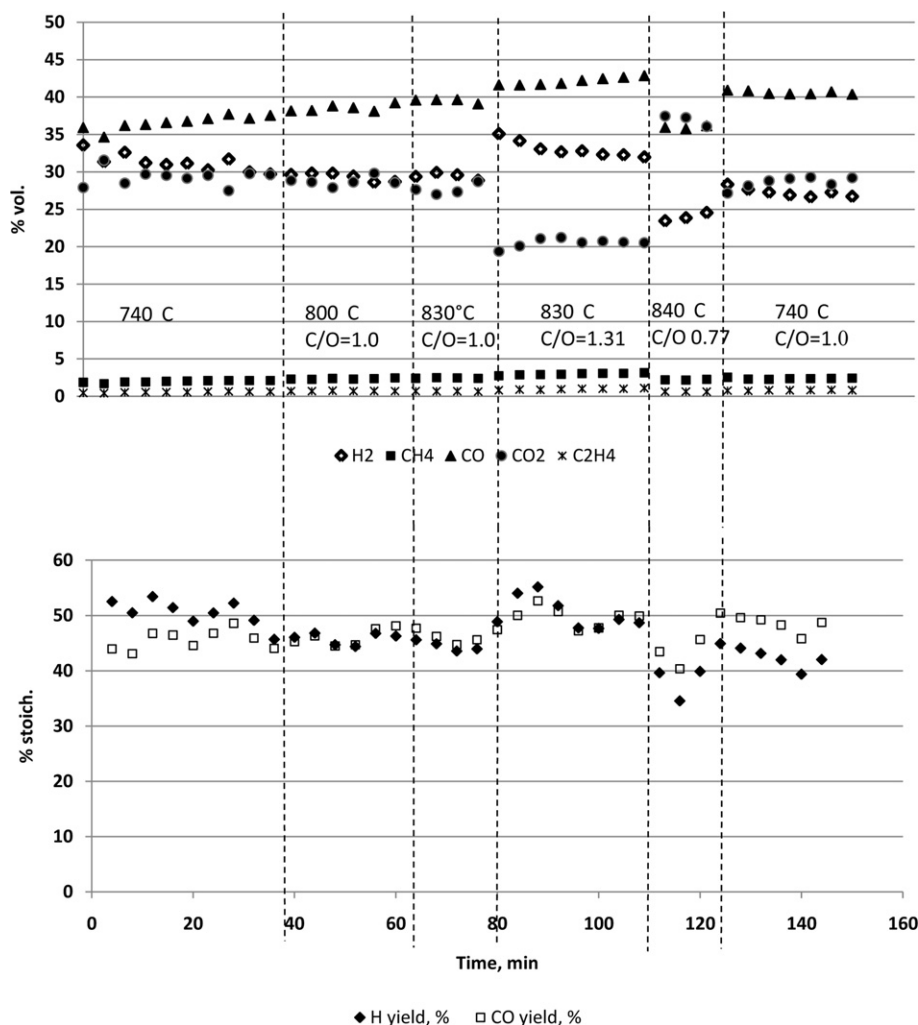


Fig. 9 – Product gas composition (nitrogen-free basis, top) and yields of H_2 and CO (bottom) from POX of bio-oil at different process conditions.

4.1. Efficiency and syngas production

Direct CPO of bio-oils resulted in almost complete bio-oil carbon-to-gas conversion, but despite longer residence time,

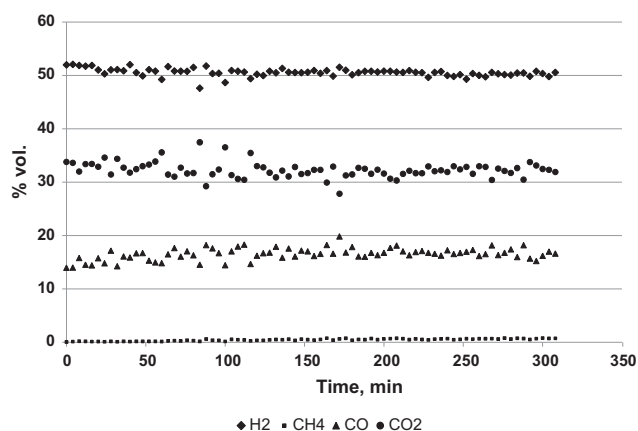


Fig. 10 – Product gas composition from POX/steam reforming of poplar bio-oil/methanol (90/10 wt%).

it reached only 83% in the staged reactor. The likely reason is that O_2 was almost totally consumed during the non-catalytic reaction occurring in the freeboard, which made it unavailable for the following catalytic oxidation. Therefore, probably only the volatile bio-oil compounds reacted with O_2 in gas phase and the less volatile components mostly formed deposits on the catalyst because there was not enough oxidant to react with. However, the H_2 yield produced in this reactor was higher than in DCPO. The oxidation in the freeboard probably favors complete oxidation, decreasing total conversion. However, by preserving the active catalyst for SR and WGS, H_2 yields increase. By contrast, DCPO utilizes more catalyst for oxidation, assuring higher total conversion but quenching some of the WGS and reforming, both by competing oxidation reaction and deactivation due to coke and impurities deposition.

The yield of H_2 from autothermal partial oxidation of pyrolysis oils is much lower than from steam reforming of the same compounds. This is a natural result of the differences between oxidative Equations (2) and (3) and reforming Equation (1). The tradeoff is in energy demand, thermal efficiency, and coke management. For methane CPO, despite similar kinetics in dilute concentrations, oxidative chemistry is faster than steam

Table 2 – Experimental (Exp) and calculated (Thr) yields and concentrations for selected data points.

FUEL	Poplar		Poplar		Poplar*		Poplar*		Pine		Pine		Hardwoods	
t (s)	0.053		0.030		0.190		0.190		0.039		0.046		0.051	
GHSV (hr ⁻¹)	22000		37000		11000		11000		29000		26000		17000	
Heat Source	autothrml		autothrml		furnace		furnace		autothrml		autothrml		furnace	
Backface Temp	651		684		740		750		666		614		950	
S/C (S/C)	0	(0.1)	0	(0.1)	0	(0.2)	1.4	(1.6)	0	(0.9)	0	(1.0)	0	(0.4)
C/O	0.97		0.85		1.0		1.16		0.47		0.47		1.10	
λ	0.37		0.46		0.44		0.38		0.78		0.84		0.40	
Bio-oil wt%	45		50		90		90		82		86		80	
Methanol wt%	45		50		10		10		0		0		20	
Methane wt%	10		0		0		0		18		14		0	
Bio-oil C%	47		56		92		92		58		64		83	
Methanol C%	37		44		8		8		0		0		17	
Methane C%	16		0		0		0		42		36		0	
Concentration (Dry, N ₂ free %)	Exp	Thr	Exp	Thr	Exp	Thr	Exp	Thr	Exp	Thr	Exp	Thr	Exp	Thr
H ₂	22	51	27	46	27	40	51	48	11	31	28	26	26	40
CO	51	28	42	26	41	36	17	17	32	9	15	5	58	41
CH ₄	13	2	2	0	3	0	0.5	0	15	0	2	0	6	0
CO ₂	13	19	28	27	29	24	32	35	42	60	55	69	9	19
C Convsrn (%)	101	100	94	100	83	100	91	100	105	100	102	100	94	100
Yield (%) H ₂	19	71	25	62	50	67	94	95	6	21	19	16	30	61
CO	65	57	54	49	46	60	31	33	37	13	21	7	73	69
CH ₄	17	3	3	0	2	0	1	0	17	0	2	0	8	0
CO ₂	17	40	36	51	36	40	59	67	50	87	79	93	12	31

A * indicates the use of a freeboard prior to the catalytic region. S/C is given as defined above, without considering water in the fuel; (S/C) reports the total ratio counting water in the bio-oil. The derivatives of fuel carbon are given as a percent. For example, Bio-oil C% refers to the carbon fraction of the total fuel originating in the given type of bio-oil. Conversion of carbon species is given by C Convsrn (%). Values >100%, are likely due to experimental error, though a small amount may also be attributable to the cleansing of some coke that was deposited before the reactor achieved steady state.

reforming under competitive conditions [37]. The lower activation temperature for oxidation [39] underscores faster kinetics for bio-oil as well. These observations suggest some oxidation can be useful for maintaining a clean reactor and catalyst; combining this with some external heating and steam addition may achieve the additional benefits of higher H₂ production. Rioche et al. introduced O₂ in sufficient quantity to examine autothermal reforming, but the high S/C = 10.8 required a large quantity of O₂ which oxidized part of the H₂ product [21]. Similarly, the high water content of the pine bio-oil in this study acted as a significant heat sink, requiring a high degree of oxidation in order to achieve autothermal operation. This is evident in the comparatively low C/O and high λ in Table 2.

The optimum for H₂ production is an autothermal POX/SR process that provides more H₂ than POX and does not require external heat. In the laboratory system, heat was supplied by electric furnace to offset high losses. However, for the same flow proportions of bio-oil, air, and steam as used in the experiments, a larger reactor operating with heat losses <10% would not need external heat.

The yield of H₂ in the DCPO reactor is low compared to that predicted by equilibrium calculations. As described above, oxidation is fast with respect to steam reforming under reaction conditions on Rh catalysts. This oxidation may preferentially occupy surface sites, impeding the effect of steam reforming. As a result, unmeasured H₂O yields are over the

predicted amount. Interestingly, the POX/steam reforming carried out in a larger reactor exhibited higher H₂ yield than the DCPO system. The reason could be higher temperature, longer residence time, and more active WGS and SR catalyst than in the DCPO reactor. Loss in SR is also observed as a consequence of deactivation, eg. due to sulfur impurities [40].

WGS is also responsible for H₂ production and is typically equilibrated on a healthy Rh–Ce, washcoated catalyst [41]. In most of these DCPO experiments, WGS is certainly not equilibrated: an abundance of CO (and implicitly, water) is reported (Table 2), while a deficiency in CO₂ and H₂ are apparent. By contrast, the staged-catalytic experiments are much nearer equilibrium.

Both reactor configurations overproduce CH₄. Methanation can consume H atoms at the cost of H₂. In all cases where CH₄ was added to the reactor, an abundance of CH₄ is measured in the effluent. However, CH₄ is also above equilibrium (albeit not as high) in all cases for which methane is not added as a portion of the fuel, and increases steadily in the POX experiments.

4.2. Challenges

The loss of WGS activity, steam reforming, and an increase in methanation all indicate deactivation of the catalyst in the DCPO experiments, a problem that can be largely mitigated by an upstream freeboard. Although the catalysts were still

functional and clean of coke, they apparently do not compare in activity to those used for similar reaction of model compounds [29–31]. Maintaining healthy noble metal catalysts is an important research goal for catalytic upgrading of bio-oils that sophisticated reactor design may achieve. An advantage of the staged reactor design is that it allows the primary reaction to occur non-catalytically, drastically increasing the lifetime of the catalyst, which is used to increase H_2 production and overall conversion.

Two challenges affect reactor design for upgrading pyrolysis oil. As depolymerized, dehydrated plant matter, many of the constituents of pyrolysis oils have a tendency to polymerize over time [33,34]. This polymerization is accelerated at higher temperature (typically temperatures in excess of 80 °C are quoted in the literature), and the dehydration of pyrolysis oils to form char is a significant consideration for thermal upgrading processes at operating temperatures. Second, although pyrolysis oils contain significantly less ash than biomass, the deactivation of catalysts due to inorganic deposition is a major reactor design hurdle for processing bio-oils.

For the first challenge, sophisticated reactor design can alleviate char formation between pyrolysis oil introduction and catalysis. Char forms from pyrolysis oils (and from biomass) at long exposure to low heating rates; gasification occurs at high temperature with fast heating rates [42]. Thus, extremely rapid heat transfer is essential to achieve gasification temperatures without char formation. In the case of DCPO, this requires introducing the fuel at room temperature and bringing it to reaction temperature, >700 °C, within a few milliseconds. Catalytic reactors are well equipped for the task of achieving high heat transfer rates because the reactant directly contacts a hot solid catalyst. The staged reactor design achieves high heat transfer rates by utilizing small particle sizes and preheating reactants, eg. steam. Thus, rather than requiring heat transfer to the whole reactant fluid, heat transfer is only necessary to small droplets from the hot gases. Moreover, exothermic oxidative chemistries are particularly well suited to high heat transfer rates as the heat is produced directly at the reaction site, be it catalyst or free-board. For these reasons, oxidation, and especially catalytic oxidation has greater potential for low coke pyrolysis oil gasification than does catalytic steam reforming.

However, on a lab scale, an additional problem must be considered: Leidenfrost film boiling. On a hot catalytic surface, liquid droplets of bio-oil form a vapor phase barrier between the droplet and the catalyst that buoys up the liquid droplet. This is especially pronounced on porous surfaces, which exhibit longer droplet residence times [43]. Liquid then bounces to areas of lower temperature which, in a small reactor, include the quartz walls at the edge of the hot catalyst. Here the liquid finally achieves good thermal contact with the cooler (300–400 °C) wall. However, due to low heat transfer rates and the absence of catalyst at the wall, the liquid chars rather than breaking down to C_1 products. A furnace to heat the walls higher than the catalyst front face temperature avoids this problem. Scaling the reactor up will likely also ameliorate this problem, though perhaps a spouting or fluidized bed would be a more direct solution. In this consideration, the DCPO reactor can behave like a staged catalytic reactor.

Another solution to the formation of char is the introduction of steam. Steam requires higher temperature than O_2 to react with coke, but can be more effective [39]. Significant quantities of water are necessary to achieve steam reforming rates on par with coke formation, and this represents a thermal drag on the system. If sufficient heat is available to offset this thermal cost, steam reforming can achieve much higher H_2 production and greater conversion of pyrolysis oil to C_1 products. Insufficient heat addition eliminates these benefits of water addition, and results in extremely comparable product spectra, as depicted in Figs. 3 and 4.

The second challenge, that of ash build up, appears non-detrimental to the catalyst, at least during relatively short tests. Ash accumulates on the front face of the catalyst and can be brushed off periodically, allowing the catalyst to be reused. Many of the DCPO experiments above occurred on catalysts reused in this manner without ill result. However, the time frame for the total life of these catalysts, several tens of hours, is too short to draw meaningful conclusions about the resilience of noble metal catalysts to inorganic impurities, and the loss of WGS activity may be attributable to catalytic poisoning. Research into this question is ongoing.

Another experimental parameter in the reactor design for the above described experiments is pore diameter. Conventional wisdom and experimental evidence with bio-oil proxies indicate that smaller pores result in greater conversion to equilibrium syngas products [44,45]. However, the velocity of droplets impinging on 80 ppi catalysts requires a pressure drop that results in recirculation of the aerosol. For model compounds, this recirculation is not a major issue: the small fraction of recirculated fuel eventually deposits on the walls and slides down into the catalyst, or vaporizes on the walls and enters as a gas. However, bio-oil cannot vaporize and, given the low rate of heat transfer on the wall, readily polymerizes in such a setup. As a result, recirculation must be minimized or, at least, deposited pyrolysis oil must not form char in such a way that it clogs the reactor vessel.

One solution to this problem is to increase the proximity of the nebulizer to the catalyst, such that little or no open area exists to support the formation of coke from low heat transfer at the walls, thereby blocking the nebulizer. A second solution is to decrease the pressure drop or the velocity of the spray. Given the construction of these gas-fed nebulizers, it is difficult to decrease the velocity of the spray, though the ultrasonic nozzle circumvents this problem. Increasing the pore diameter, on the other hand, reduces the pressure drop. A series of experiments on 20 ppi, 45 ppi, and 80 ppi pore diameters indicate that a 20 ppi/45 ppi/45 ppi bed is most effective at achieving high conversion and low rates of coke formation due to upstream recirculation. Scale up is likely to improve this problem as well.

Incidentally, as this reactor is autothermal and scalable, it is conceivable to use bio-oil as a H_2 source with an on-board reformer for automotive fuel cell applications. For instance, using the second column in Table 2, the poplar blend, and assuming a top power consumption rate of 1 kg H_2 /hr for a light duty automobile [46], a reactor would require 3.7 kg of catalyst, or 37 g Rh. With improvements in WGS performance and reactor design, 14 g Rh may be sufficient.

5. Conclusions

- Pyrolysis oils can be catalytically converted to syngas for upgrading to liquid fuels. Noble metal catalysts achieve high conversion to H_2 and CO. The reaction can either proceed autothermally or higher yields can be achieved with the addition of process heat.
- Partial oxidation of poplar bio-oil generated 3 g H_2 /100 g bio-oil corresponding to about 50% of the stoichiometric yield. Additional 3 g of hydrogen could be obtained from carbon monoxide by water-gas shift.
- Addition of steam to the reactor can significantly increase the production of hydrogen. At C/O = 1.16 and S/C = 1.6, which fall into the range of autothermal process 7.2 g hydrogen was produced from 100 g bio-oil, which could increase to 9.3 g/100 g bio-oil after completing gas-water shift conversion.
- Carbon-to-gas conversion was not always complete and carbon deposits were found on the catalyst. Although the regeneration by air oxidation restored most of the catalyst activity, long-term catalyst performance tests are needed to demonstrate viability of the process.
- Coke formation is the major hurdle for reactor design, though solutions are possible with oxidation, high rates of heat transfer, and the addition of steam. Ash handling may remain a problem for direct catalytic partial oxidation, though an upstream freeboard design may ameliorate this issue.

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