

CATALYTIC PROPERTY OF OLIVINE FOR BIO-OIL GASIFICATION

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Introduction

Biomass is an attractive renewable source of fuel and energy. Thermochemical processes can convert biomass to a liquid bio-oil or to a syngas. The advantage of using bio-oil as an intermediate is that, in contrast with both raw biomass and gas, it can easily be produced in small distributed units, stored and transported. Not only can platform chemicals and clean fuels be produced from syngas, but hydrogen is itself an alternative fuel. A high hydrogen production is usually desired: for example, methanol production requires a syngas with a molar H_2/CO ratio of 2. Therefore, maximum hydrogen production has been a major objective in steam reforming/gasification of bio-oil.

An appropriate catalyst is one of the most important operating factors in syngas production. Olivine (with general formula of $(Mg,Fe)_2SiO_4$) is a mineral material that has been investigated in biomass gasification to crack tars in the product gases; it is attrition resistant in fluidized bed reactors and has catalytic activities in gasification processes because of its iron content. However, pre-treatment of olivine, particularly, calcination temperature is crucial to make it catalytically active. It has been claimed that iron content of olivine must be in the form of iron oxide when it is introduced in the gasification reactor; gases such as hydrogen and carbon monoxide, which are produced in gasification reactors, reduce the iron oxide to metal iron (Fe^0) that is an active catalyst of gasification reactions.

On the contrary, it has been seen in our catalytic bio-oil gasification tests in a pilot fluidized bed that when olivine calcined with air was used, production of hydrogen and carbon monoxide was low while production of carbon dioxide was considerably high. Therefore, a new motivation was emerged to investigate relation between pre-treatment of olivine and its catalytic activity in the micro scale Jiggle Bed Reactor setup, which was designed and developed at the institute for chemicals and fuels from alternative resources (ICFAR).

Experimental Setup and Procedures

The Jiggle Bed Reactor (JBR) is a batch fluidized bed micro-reactor where heat required by the gasification reactions is supplied by induction heating. Solid particles are fluidized in a ceramic crucible by the fast alternating vertical motion provided by a linear pneumatic actuator. The frequency of the actuator is 3 Hz and the amplitude of its motion is 0.1 m; these conditions provide smooth fluidization of the bed particles. There is a copper coil around the ceramic crucible. A high voltage current passing through the coil provides a magnetic field that induces hysteresis and eddy currents within the wires inside the crucible. The directions of the magnetic field and induced currents are alternated with a frequency of about 250 kHz. There is a very small temperature difference between the heating surface and the catalyst bed, which minimizes the parasitic thermal reactions that occur in other reactors. A schematic of the experimental setup is shown in Figure 1.

The Drummond capillary tubes with 4 μ l volume were used to inject precise amount of the bio-oil into the batch reactor.

A Varian micro GC CP4900 instrument was used to analyze the product gases H_2 , CH_4 , CO , CO_2 , C_2H_4 and C_2H_6 . This micro GC was equipped with three columns 10m MS5A, 10m PPU and 8m 5CB. Helium was used as the carrier gas in the micro GC. Since the product gases were diluted with argon in the gas sampling bag, their concentration was very low, requiring a high sensitivity setting of the TCD and a sampling time of 500 ms. Because the GC did not detect the steam in the product gases, water measurement and, hence, elemental balances could not be performed. GC runs were conducted for 3 minutes.

In order to calculate the number of moles of the product gases and the total carbon conversion, a known volume of an external standard gas was added to the mixture of product gases: 500 μ l of normal C₄H₁₀ was injected into the vacuumed gas sampling bag with a gas tight syringe. C₄H₁₀ was never produced during the gasification tests and was, thus, a suitable external standard gas. The gas sampling bag was squeezed manually for several times to ensure good mixing between the standard gas and the product gases. Experiments were repeated for 3 times to check the reproducibility of the data.

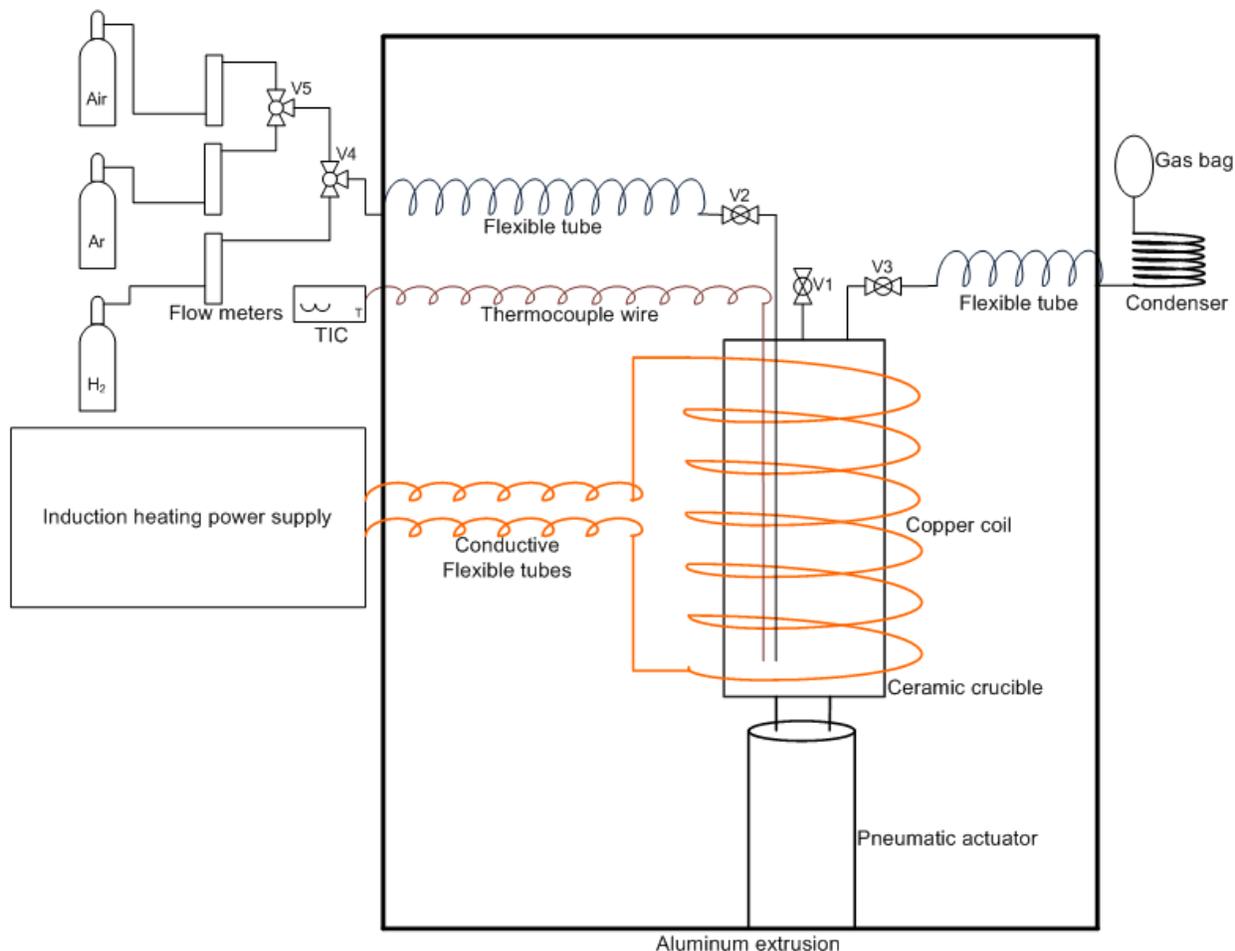


Figure 1. Schematic of the JBR experimental setup for the catalytic gasification tests

Bio-oil Characteristics

The bio-oil used in this research was produced by fast pyrolysis of hardwood at moderate temperatures, in the absence of oxygen, at the Dynamotive Energy Systems Corporation in Canada. This bio-oil had been stored in the lab for three years. As presented in Table 1, elemental composition of the fresh bio-oil was changed and therefore different from that of the old bio-oil after 3 years so that hydrogen and oxygen contents were increased with regard to carbon content. Gasification experimental work was carried out with the old bio-oil.

Table 1. Elemental analysis of the Dynamotive bio-oils

	Fresh bio-oil	Old bio-oil
H, wt%	7.20	8.04
C, wt%	41.67	36.30
N, wt%	0.27	0.30
O, wt% (balance)	51.13	55.36
Water content, wt%	24.34	27.52
General formula	CH _{2.071} O _{0.920} N _{0.0053}	CH _{2.624} O _{1.121} N _{0.0065}

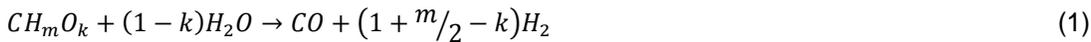
Preparation of the Bed Material

Silica sand and olivine were used as the bed materials with a size distribution of 106-212 µm. Two samples of olivine calcined at 850°C and 1000°C each for 24 hours and one sample of olivine reduced with hydrogen at 800°C for 24 hours were investigated as the bed materials in the Jiggle Bed Reactor to find out whether metallic iron (Fe⁰) or iron oxides are suitable for bio-oil gasification. The calcined samples of olivine had been placed inside a furnace to be calcined whereas the third sample had been placed in the Jiggle Bed Reactor and was reduced in situ by a 100ml/min flow of hydrogen. Since experiments were carried out at 800°C, calcination temperatures were chosen to be higher than the reaction temperature in order to obtain particles with a stable structure in the reactor. The bed mass was 10g in all experiments.

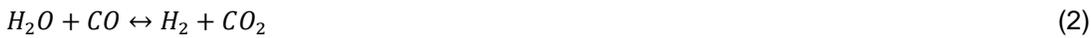
Experimental Methodology

Gasification of bio-oil in the Jiggle Bed Reactor was investigated at 800°C. The effect of the reaction time was tested at 10s, 20s, 30s, 60s, 120s and 240s, where the reaction time was the time between the feed injection and the flushing with argon of the product gases into the gas sampling bag. In order to determine the effect of the bed material on bio-oil conversion and product gases yields, silica sand and pre-treated olivine samples were used in the reactor. The Drummond capillary tubes with 4µl volume were used to introduce the bio-oil into the reactor, which did not change significantly the reactor pressure. Since it was important to know mass of the feed bio-oil for yield and conversion calculations, five capillary tubes were filled with bio-oil and then the average mass of bio-oil content in those tubes was considered as the mass of bio-oil equivalent to a 4 µl volume. To make sure experimental data were reproducible, experiments were repeated 3 times. Yield data reported in this paper are in fact average values of the obtained experimental yield data. Maximum spread between the replicate data was ±4%.

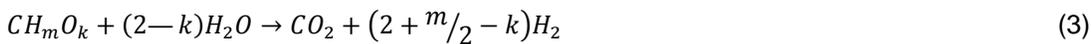
In the presence of steam, bio-oil with general formula of CH_mO_k (neglecting the nitrogen content) can be converted to syngas (H₂+CO) according to reaction 1:



If there was enough steam in the reactor, the produced CO would react with steam through the water-gas shift reaction to produce more hydrogen:



Therefore, summing up reactions 1 and 2, the overall steam reforming of bio-oil can be expressed by reaction (30):



There are a number of other reactions taking place after bio-oil is injected into the reactor. In this research we did not add additional water because in industry, the practice is to use a separate water-gas shift reactor, downstream of the gasification reactor, which can be operated with a temperature and a catalyst that are optimized for the water-gas shift reaction. In other words, our goal was to maximize the conversion of bio-oil to product gases and conversion of the hydrogen contained in the raw bio-oil, including its own water, to hydrogen gas (H₂). Therefore, the yield of produced hydrogen was defined according to equation (4):

$$Y_{H_2} \left(\frac{g}{g} \right) = \frac{\text{mass of hydrogen as H}_2 \text{ in product gas}}{\text{mass of H in the raw bio-oil}} \quad (4)$$

To estimate the number of moles of the bio-oil, bio-oil with a general formula of CH_mO_k was assumed from its elemental composition. Since maximum 1 mol of a product gas like CO, CO₂ and CH₄ can be produced per 1 mole of the injected bio-oil, yield of these gases were estimated as:

$$Y_{CO,CO_2,CH_4} \left(\frac{mol}{mol} \right) = \frac{\text{moles of the product gas}}{\text{moles of the bio-oil}} \quad (5)$$

Accordingly, yields of C₂H₄ and C₂H₆ hydrocarbons were estimated by equation 6:

$$Y_{C_2H_4,C_2H_6} \left(\frac{mol}{mol} \right) = \frac{\text{moles of the product gas}}{0.5 \times \text{moles of the bio-oil}} \quad (6)$$

The carbon conversion was calculated by summing up the yields of carbon containing product gases. Mole fraction of the product gases was assumed as their concentration in the mixture of the detected product gases for the thermodynamic analyses.

Results and Discussion

A thermodynamic model was developed in this research to compare experimental mole fraction of the product gases obtained with different bed materials at the same operating conditions with the equivalent predicted equilibrium mole fractions.

Figure 2 illustrate the evolution with reaction time of the experimental mole fraction of the product gases, with different bed materials. Also, a horizontal line indicates equilibrium mole fractions calculated by the thermodynamic model. It must be pointed out that the estimated equilibrium mole fractions of the product gases are expressed on a dry basis to be able to compare them with the experimental data. With the exception of the silica sand for which experiments were conducted also at a reaction time of 600s, experiments were carried out at reaction times of 10s, 20s, 30s, 60s, 120s and 240s for all the tested bed materials.

With the reduced olivine, it is clear that the product gases reach mole fractions near the equilibrium values even at the shortest reaction times. This means the reduced olivine acted as an active and effective catalyst that greatly speeded up the reactions.

With sand, the mole fractions of the product gases reached their equilibrium values, but at much longer reaction times. A reaction time of 600s was, then, required to reach the mole fractions that were achieved in about 20s with the reduced olivine.

With the calcined olivines, the mole fractions of the product gases, especially, hydrogen, CO and CO₂ were far from the equilibrium values. It is seen that the mole fractions of hydrogen, CO and hydrocarbons decrease with increasing reaction time and drop below the equilibrium mole fractions whereas the mole fraction of CO₂ increases with increasing reaction time and is always above the equilibrium mole fraction. Since the equilibrium mole fractions were calculated according to the elemental composition of the raw bio-oil, this suggests that the calcined olivine acts as an extra source of oxygen in the reactor, which can lead to a large production of CO₂ and steam. This hypothesis is confirmed by the XRD plots (not shown in this abstract), which show that α-Fe₂O₃ was formed on the olivine calcined at 1000°C. Such oxide phases should have been also formed on the olivine calcined at 800°C although it was not detected by XRD; therefore, in the presence of reducing gases such as hydrogen in the reactor, iron oxides can be reduced, providing an additional source of elemental oxygen.

Elemental analysis of the original olivine, the olivine calcined at 800°C and the olivine calcined at 1000°C by a CHNOS elemental analyzer showed that oxygen content of the calcined olivines had increased relatively

compared to the original olivine so that the largest oxygen content was in the olivine calcined at 1000°C. It seems that the calcined olivine works like an oxygen sponge so that the released oxygen reacts with the combustible product gases.

Regarding the positive effect reported in the literature for calcined olivine in continuous processes, it may be that the calcined olivines were inappropriate catalysts in our batch jiggle bed reactor because of the small bio-oil to catalyst ratio.

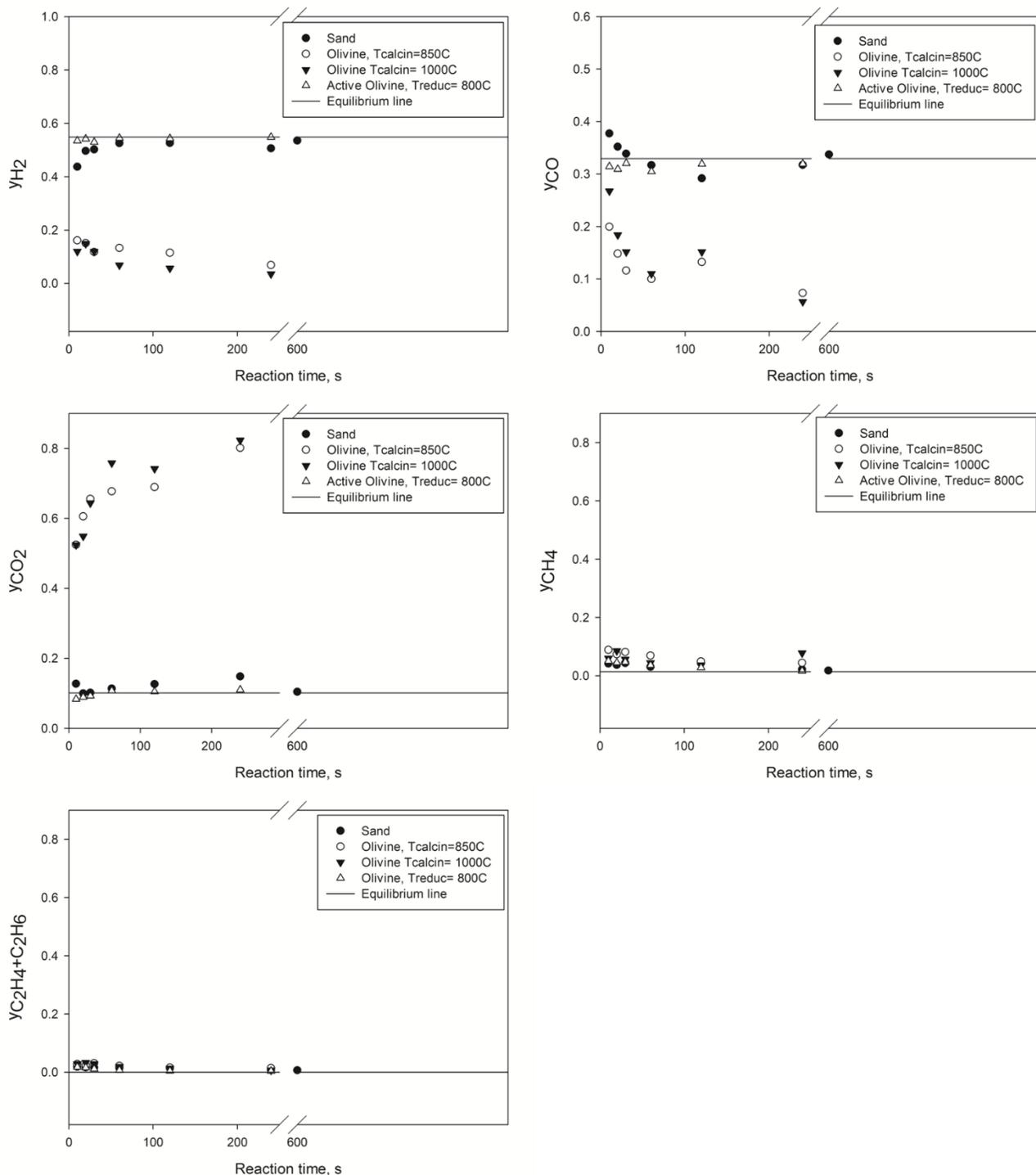


Figure 2. Measured mole fraction of product gases compared to predicted equilibrium mole fractions, on a dry basis. Bed materials: olivine and sand. Temperature: 800°C

Since the molar H_2/CO ratio is a key parameter that is essential for downstream processes, the equilibrium model is a useful tool to predict this ratio on the basis of elemental analysis of the feedstock. Figure 3 illustrates the predicted molar H_2/CO ratio at equilibrium that is expected from gasification of the Dynamotive bio-oil. It was reached in 30s with the reduced olivine and in 60s with the inert sand. However, a reaction time of 60s would not be suitable with sand because full carbon conversion of the bio-oil might not be obtained even at much longer reaction times.

The predicted molar H_2/CO ratio was 1.65 without the addition of extra steam. The addition of steam would be required if a high value of the molar H_2/CO ratio, such as 2, was required for the downstream process. According to the developed thermodynamic model, it was estimated that a molar H_2/CO ratio of 2 can be obtained at 800°C when additional 0.344g steam per g of bio-oil is injected into the reactor.

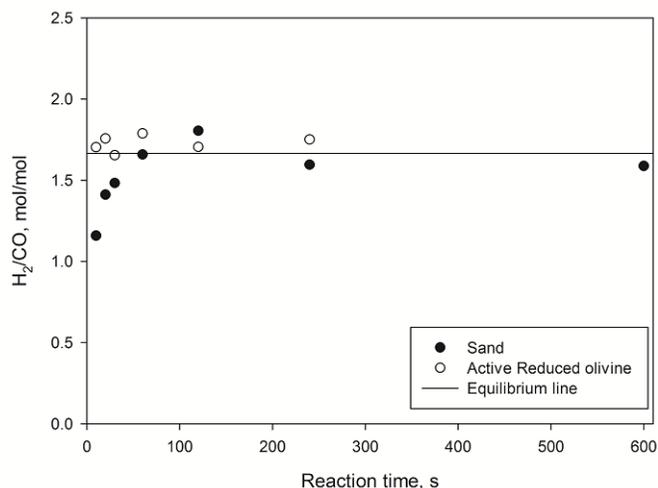


Figure 3. Experimental molar H_2/CO ratio versus predicted molar H_2/CO ratio at equilibrium. Bed materials: olivine and sand. Temperature: 800°C

Conclusions

Despite the literature reports claiming that calcined olivine is a promising biomass gasification catalyst to crack tars and to achieve a high hydrogen yield, experimental data in this research revealed that calcined olivines were inappropriate because oxygen is released from such olivines under gasification conditions. On the other hand, it was discovered that if olivine was reduced in-situ with hydrogen, free iron metals are on the olivine that make it a very active catalyst that results in complete carbon conversion of the bio-oil and a high hydrogen yield at relatively short reaction times.

The developed thermodynamic model confirmed that calcined olivines were inappropriate in bio-oil gasification. Product gases produced with the reduced olivine and silica sand, on the other hand, reached the predicted equilibrium concentrations. Since the reduced olivine is a very active catalyst, equilibrium was reached quickly, but took a much longer time with the inert silica sand.

It was also estimated by the thermodynamic model that maximum molar H_2/CO ratio that can be achieved through gasification of the Dynamotive bio-oil in the absence of additional steam is 1.65. According to the model, to reach a molar H_2/CO ratio of 2 would require the addition of 0.344g of additional water per g of bio-oil.