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Jiggle bed reactor for testing catalytic activity of olivine in bio-oil gasification

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ABSTRACT

The Jiggle bed reactor (JBR) is a new batch-wise micro fluidized bed reactor that was designed for screening the catalysts at various gasification operating conditions. Natural olivine mineral, $(\text{Mg,Fe})_2\text{SiO}_4$, was selected as a suitable catalyst for bio-oil gasification in fluidized bed reactors due to its iron content and its attrition-resistance property. However, because iron can be present in the form of different phases in the olivine structure, e.g. iron oxide or metallic iron, a clear understanding of the link between the iron phase and catalytic activity of olivine is essential. Therefore, three pre-treated olivine samples were prepared as the bed material for catalytic tests in the JBR: calcined with air at 850 °C and 1000 °C and reduced with hydrogen at 800 °C. Silica sand was also utilized as an inert bed material for non-catalytic tests. A thermodynamic model was developed to predict the products mole fraction at equilibrium as a basis to evaluate behavior of the bed materials.

Results proved that olivine was an active catalyst for bio-oil steam gasification when it was reduced with hydrogen, due to the presence of iron metal, on the contrary to calcined olivines that released oxygen, due to the presence of iron oxide, which reacted with the combustible products. According to thermodynamic analysis, the product gases reached predicted equilibrium state in the case of the reduced olivine despite the event of the calcined olivines. On the other hand, the activity of the calcined olivine samples revealed that such materials might have promising potentials to be applied in chemical looping gasification processes.

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1. Introduction

There are some drawbacks attributed to utilization of the conventional fossil fuels such as petroleum oil, natural gas and coal to produce heat and valorized chemicals. For instance, they are limited energy resources, and their conversion processing generates harmful emissions, e.g. CO_2 , SO_x and NO_x , leading to a rise in human health, environmental and global warming problems. Development of viable and profitable processes to substitute fossil fuels with renewable resources has been severely practiced in the last decades, particularly, in countries that have to import fossil fuels. Processing the renewable energy resources provides advantages such as reduction of greenhouse gas emissions to stay with environmental rules as well as fuel supply security and reduction of fossil fuel imports.

Biomass is an attractive renewable source of fuel and energy. Thermochemical processes can convert biomass either to a liquid bio-oil, bio-char and gases through flash pyrolysis [1–10], for instance, or to a

syngas [11–22]. Syngas, which is a mixture of hydrogen and carbon monoxide [23] can also be produced from gasification of bio-oil [24–34]. In fact, there are some advantages by conversion of biomass to bio-oil and then conversion of bio-oil to syngas: bio-oil, for instance, can be consumed directly as a fuel or upgraded to chemicals and fuels. As an economic advantage, in contrast with both raw and bulky biomass and gas, the transportation cost will be considerably saved if the dense bio-oil is produced in small-distributed units, stored and then transported to a syngas production plant at a central bio-refinery. It is also noteworthy that all primary, secondary and tertiary tar compounds that will have detrimental effects on the downstream equipment are produced through direct gasification of biomass to syngas whereas tertiary tars are not produced through gasification of bio-oil to syngas [35].

Syngas is an essential building block chemical mixture. 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 primary objective in steam reforming/gasification of bio-oil.

Despite hydrocarbons that typically contain carbon and hydrogen and to some extent sulfur, a bio-oil is a carbon-hydrogen-oxygen bearing fuel. This elemental composition is due to its oxygenated contents

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such as organic acids, aldehydes, alcohols, ketones, furans as well as phenolic and cyclic oxygenates along with 20–40 wt% water [36–38]. The composition of the mentioned oxygenates varies from a bio-oil to another depending on the upstream biomass pyrolysis conditions and type of the biomass. Accordingly, the required operating conditions to produce syngas in a bio-oil gasification process depend on its feedstock, i.e. bio-oil composition.

Despite the presence of oxygenates in a bio-oil, as discussed in Section 3, some steam is required in favor of maximum production of hydrogen and carbon monoxide. In other words, if the water content of bio-oil is not enough, excess steam should be consumed in the gasifier to reach the desired H₂/CO ratio.

In addition to steam, an appropriate catalyst is required in bio-oil gasification. Moreover, reactor design in which a sufficient gas-solid contact should be maintained contributes significantly to the efficiency of the process [39]. For instance, due to poor gas-solid contact and non-uniform temperature profile in a fixed bed reactor, severe coke formation occurs on the surface of catalysts leading to fast catalyst deactivation [28,40]. Therefore, fluidized bed reactors are preferred to fixed bed reactors because they provide enhanced heat and mass transfer conditions. On the other hand, since much smaller particles of a catalyst are employed, particles attrition and entrainment are problematic in a fluidized bed reactor that may result in catalyst loss [41].

So, it is very crucial to find and employ an appropriate catalyst with an optimum formulation and physicochemical properties, which provides the required activity for maximum conversion of bio-oil and yield of syngas, while it has high stability against deactivation and attrition in fluidized bed reactors. Therefore, sometimes an array of different catalysts must be investigated for a given bio-oil. On the other hand, testing catalysts with new formulations and physicochemical properties under different gasification operating conditions such as temperature, reaction time and steam to carbon ratio in a pilot-scale fluidized bed reactor is indeed costly and time and labor demanding. These problems are, particularly, because there are limitations in bio-oil supply to a large scale and long term stability of bio-oil in the storage [38,42–49]. Thus, utilization of a micro reactor to screen the array of the catalysts is advantageous concerning cost, time and labor.

There are some drawbacks with the available micro reactors, particularly, to test endothermic gasification reactions, and as a result, operating conditions in the large scale fluidized bed reactors cannot be mimicked in such reactors [39,50]. For instance, since they employ an external furnace to supply the heat, i.e. heat is transferred from the reactor wall to the bed, there is a high temperature gradient in the bed, heat transfer coefficient is slight and parasitic thermal cracking reactions occur on the wall. Besides, because agitators are employed to circulate the gas in the reactor, the hot gas may leak out.

Therefore, the jiggle bed reactor (JBR) that is a batch-wise fluidized bed micro reactor was designed and developed at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR) to overcome the above mentioned challenges with the pilot plant setups and the micro reactors.

The synthesized nickel based catalysts supported mostly on alumina have been investigated for conversion of bio-oil or its model compounds [29]. There are also some natural minerals that have potentials to be employed as a catalyst. As such, olivine is a mineral that has been investigated by several researchers to crack the tars, produced during biomass gasification, in the product gases [51–59]. It has been shown that olivine, with general formula of (Mg,Fe)₂SiO₄, has enough strength against attrition in a fluidized bed reactor, and its iron content makes it a suitable catalyst for gasification processes [60–62].

Since different phases of iron, e.g. metallic iron, FeO, Fe₂O₃, Fe₃O₄ and MgFe₂O₄, can be present in the structural matrix of olivine, it is important to understand that how iron behaves as a catalyst in the catalytic gasification tests. In other words, proper pre-treatment of olivine is required to provide the catalytically active phase of iron in the reactor. However, this process is not very well discussed in the literature.

It has been proposed based on some temperature programmed reduction (TPR) tests that if olivine were pre-calcined with air at an optimum temperature, a maximum amount of iron oxide would come off the bulk of olivine. So when it is introduced into the gasification reactor, gases such as hydrogen and carbon monoxide, which are produced in the reactor, reduce the iron oxide to metal iron (Fe⁰) that is an active catalyst for gasification reactions [55]. However, we have seen in our catalytic bio-oil gasification tests in a pilot fluidized bed reactor that when the calcined olivine material was loaded into the reactor, production of hydrogen and carbon monoxide was low while production of carbon dioxide was considerably high. Therefore, a new motivation was emerged to investigate the relation between pre-treatment of olivine and its catalytic activity in bio-oil gasification.

We employed the jiggle bed reactor (JBR) to perform catalytic tests on different pre-treated olivine samples, two samples of calcined olivine and one sample of reduced olivine, to monitor their activity in the gasification environment. Also, a thermodynamic model based on equilibrium constant of the independent reactions between the gasification products was developed to solidify the experimental observations.

2. Materials and methods

2.1. Bio-oil characteristics

Dynamotive Energy Systems Corporation in Canada supplied the bio-oil that was produced by fast pyrolysis of hardwood. Since we had stored the bio-oil in the lab for three years, we rechecked whether its elemental composition was as of the received bio-oil. Table 1 illustrates that the elemental composition changed over the time; this could be due to either moisture absorption, loss of volatile organics or reaction with oxygen of the lab ambient [40]. Although it is far from the scope of this research, aging and change of the bio-oil composition (elemental and molecular) should be investigated to find out an optimized storage condition. Nonetheless, we utilized the old bio-oil for gasification tests of this research.

2.2. Preparation of the bed material

We employed silica sand and olivine as the bed materials with a size distribution of 106–212 μm. We prepared three pre-treated olivine particles: two samples of olivine calcined with air at 850 °C and 1000 °C each for 24 h and one sample of olivine reduced with hydrogen at 800 °C for 24 h. The olivine calcination took place inside a tubular furnace. To avoid its re-oxidation happening, the olivine reduction occurred in the jiggle bed reactor in situ by a 100 ml/min flow of hydrogen; afterward, we kept the bed under argon until before doing a reaction test. Pre-treatment temperatures were chosen to be higher than the reaction temperature in order to obtain particles with a stable structure in the reactor.

Silica sand was also utilized to carry out thermal cracking tests under similar operating conditions to compare the yield data with the yield data from the catalytic tests.

The bed mass was 10 g in all gasification trials.

Table 1
Elemental analysis of the Dynamotive bio-oil.

	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}
C/H, mol/mol	0.48	0.38
C/O, mol/mol	1.09	0.87

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