Production of syn gas / high Btu gaseous fuel from the pyrolysis of biomass derived oil

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Depletion of fossil fuels is creating opportunities in exploring alternative sources of energy. Biomass materials, being renewable and CO₂ neutral have attracted attention as a potential source of energy. At present, technologies exist to pyrolyze biomass to produce a liquid product, namely, biomass-derived oil (BDO). This BDO has found a variety of applications in various areas. In this investigation, we have carried out a systematic study on the pyrolysis of biomass-derived oil at various temperatures. Experiments were carried out in an Inconel tubular reactor. BDO was fed at a flow rate of 4.5 to 5.5 g/h along with nitrogen (18-54mL/min) as a carrier gas. The gas product essentially consisted of H₂, CH₄, CO, CO₂, C₂, C₃, C₄⁺ components. Composition of various gas components ranged between: Syn gas 17-26 mol%, CH₄ 21-27 mol% and C₂H₄ 23-31 mol%. Heating values ranged between 1300 – 1700 Btu/SCF. Additional results along these lines also will be presented. Thus, the present study shows that there is a strong potential of making syn gas, methane, ethylene and high heating value Btu gas from the pyrolysis of biomass-derived oil.

Introduction
The gradual shortage of oil reserves has created considerable interest in using alternative source of energies, which are renewable in nature. For example, the renewable energy technologies (RET) of the European commission have the target of doubling their contribution from the present 5.6% to about 12% in future. Amongst all the renewable energy sources, biomass represents the highest potential and will play a vital role in near future. Two approaches namely pyrolysis and gasification of biomass have been attempted to convert biomass into useful form of energy. The pyrolysis process is generally carried out by subjecting the biomass to high temperature under inert or oxygen deficient atmosphere. The fast pyrolysis process of biomass generally gives three products viz. gas, bio-oil (or bio-mass) and char. The bio-oil thus produced contains unsaturated hydrocarbons and is thus highly unstable. Therefore, an attempt has been made in this research to produce cleaner fuels including hydrogen, syn gas and high Btu gases from the BDO.

Experimental
The BDO was obtained from Dynamotive Technologies Corporation, Vancouver, BC, Canada. The experimental set-up used in these experiments consisted of an Inconel tubular reactor (12.7 mm i.d. and 200 mm long) containing quartz chips, through which an inert gas such as nitrogen was passed until the desired reactor temperature was reached. Then the flow rate of nitrogen was maintained at 18-54 ml/min. BDO was pumped at the rate of 4.5-5.5 ml/hr where as the reactor temperature was varied in the range of 650 to 800 °C. Each experiment was performed only for a period of 30-45 min. The product gas was cooled with a water-cooled heat exchanger and then with ice bath (to liquefy the condensable) before it was collected over saturated brine solution. The amount of the product gas was also measured for each experiment, and was analyzed for its compositions using two GCs (Carle GC-500 series and HP5890). The HP GC was equipped with a thermal conductivity detector and chromosorb 102 column for the analysis of H₂, CO, CO₂ and CH₄ where as the Carle GC, equipped with a flame ionization detector and a capillary column, analyzed hydrocarbons.
Results and Discussion
In this research the effects of reactor temperature and the nitrogen flow rate on the bio oil conversion and product gas composition was studied. The material balance for each experiment was found to be between 92-98%.

Effect of nitrogen flow rate: The effect of nitrogen flow rate on the conversion of bio-oil, yield of gas and composition of gas has been studied by changing it from 18–54 mL/min keeping pyrolysis temperature and flow rate of bio-oil constant, respectively, at 800 °C and 4.5ml/hr. It is seen that at a nitrogen flow rate of 30 mL/min and 800 °C, BDO conversion of 83wt% to gas and char was achieved. It was also observed that with the flow rate of nitrogen, the amount of gaseous product was also increased. For example, 39 l and 65 l of product gas were obtained at N2 flow rate of 18 and 54 ml/min, respectively. The effect of nitrogen flow rate on product gas composition was also evaluated. It was observed that the production of hydrogen remained almost constant with the increase in nitrogen flow rate from 18 to 45mL/min. However, there is a sharp increase in the hydrogen production with further increase in the nitrogen flow rate. CO gas yield was increased when the nitrogen flow was increased from 18 ml to 54 ml and reached maximum for N2 flow of 42 - 54 mL/min. The total amount of synthesis gas (hydrogen and CO) also followed a similar trend. The formation of methane was high at lower nitrogen flow rate. The effect of nitrogen flow rate on the production of other gases such as ethane and higher hydrocarbons was not very significant. The production of olefins (ethylene and propylene) initially after showing a slight increasing trend followed a decreasing pattern. The olefin content (predominantly ethylene) of as high as 40mol % was obtained corresponding to a nitrogen flow rate of 25ml/min. The conversion of bio-oil, olefin yield, and total Btu value of product gas were as high as 83wt%, 43 mol%, and 1738 Btu/scf, respectively. However, the syn gas yield of 65mol% was optimum at nitrogen flow rate of 54 mL/min at 800 °C.

Effects of temperature: The effect of temperature (650-800 °C) on the conversion of bio-oil, production of gas and its composition has been studied keeping nitrogen flow rate and bio-oil flow rate constant respectively, at 30 mL/min and 4.6 g/hr. The results showed that as the temperature was increased from 650 to 800 °C, the conversion of bio-oil to gas and char increased from 57 to 83 wt%. Also, as expected, the production of gas increased with temperature. For example, 26 l to 45 l of product gas were obtained when temperature was increased from 650 to 750 °C at constant N2 flow rate of 30 ml/min. However, beyond this temperature, its effect on the gas production was negligible. The effects of reaction temperature on the product gas composition were analyzed. It was observed that the concentrations of methane, olefins and Btu value were increased from 22 to 27mol%, from 30 to 34mol% and from 1300 to 1700 Btu/scf with increase in temperature from 700 to 800 °C. However, syn gas production decreased by 20mol% in spite of higher production of hydrogen with temperature. The increase in hydrogen production with temperature occurred probably because at high temperatures, breakage of the BDO sub-units evolved more hydrogen and the aromatic rings were rearranged and condensed releasing H2. Methane was formed due to the reaction between H2 and carbonaceous material.

Conclusions
The present study identifies the pyrolysis of BDO as source of gaseous fuel. It can be utilized for producing hydrocarbons and synthesis gas for various applications. By adjusting the parameters such as flow rate and temperature, the composition of the product gas from BDO can be tuned in the desired direction. A large amount of total product gas could be obtained from BDO at 800 °C, N2 flow rate of 30 mL/min and BDO flow rate of 4.6 g. In this process, the product gases essentially consisted of H2, CO, CO2, CH4, C2H4, C2H6, C3H8, and C4+ indicating it is worthwhile to proceed for gasification of BDO as a source for the production of hydrocarbons, and synthesis gas.