

**UNIVERSITY OF CENTRAL FLORIDA**

***Integrated Florida Bio-Energy Production with Carbon Capture and Sequestration***

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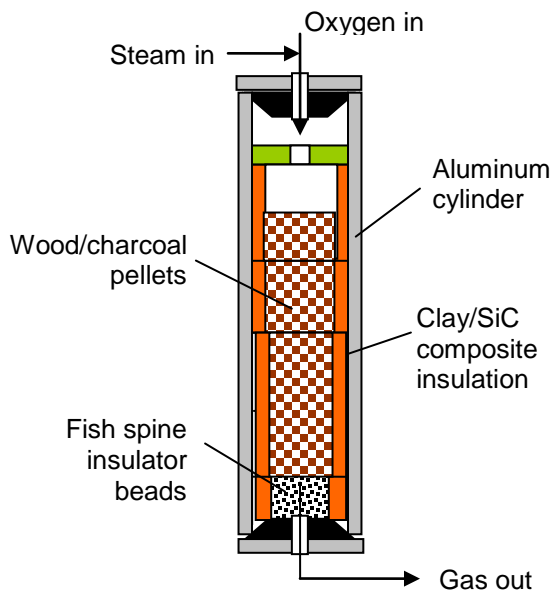
**Description:** The aim of this project is to produce liquid hydrocarbon fuels derived from Florida’s biomass resources utilizing a two-step thermocatalytic process. In the first step, biomass or biomass-derived pyrolysis oils are gasified with oxygen and steam to synthesis gas (syngas) comprised of mostly hydrogen, carbon monoxide and carbon dioxide. The oxygen source for gasification process is provided by a number of methods, *e.g.* oxygen concentrator, electrolytic unit, etc. Use of pure (or nearly pure) oxygen, instead of air, for gasifying biomass improves overall process energy conversion efficiency by reducing dilution of gasifier output gas with nitrogen. In the second step, syngas from step 1 is fed into a Fischer Tropsch (FT) synthesis unit and converted to liquid hydrocarbon fuels, *e.g.*, diesel fuel. The process can be employed with any lignocellulosic material including crop residues, forest waste, yard clippings, and energy crops. The technology also provides a means for sequestering carbon in the form of a high-value soil enhancing bio-char (terra preta) by simple modification of the gasification step 1.

**Budget:** \$425,506

**Universities:** UCF/FSEC

**Progress Summary**

A small-scale gasifier was fabricated and tested using pine wood charcoal pellets as feedstock and oxygen and steam as the gasification agents. **Fig. 1** depicts the schematic diagram of a small-scale gasifier that was used in the gasification experiments. The small-scale gasifier was fabricated using a 4” ID aluminum pipe plugged at both ends with two rubber stoppers and end plates as shown in **Fig. 1**. Specially made clay/SiC composite insulating sleeves were placed inside the reactor to provide thermal insulation.



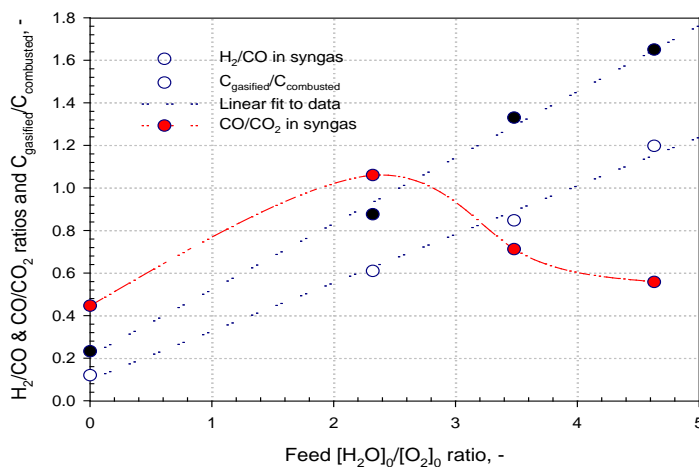
**Fig. 1 – Schematic diagram of the small-scale oxygen gasifier.**

The gasifier operated in top-lit downdraft mode using a mixture of O<sub>2</sub> and steam as oxidizers - introduced from the top. The output gas exited from the bottom of the gasifier. The main objective of the gasification

experiments reported here was to determine the effect of  $O_2$  flow rate and inlet  $[H_2O]_0/[O_2]_0$  ratio on the performance of the gasifier and quality and composition of the producer gas.

**Fig. 2** shows the effect of input  $[H_2O]_0/[O_2]_0$  feed ratio on the exit gas composition expressed as  $H_2/CO$  and  $CO/CO_2$  ratios. The data indicate that increasing the  $[H_2O]_0/[O_2]_0$  ratio increases  $H_2/CO$  in the exit gas monotonically while the  $CO/CO_2$  ratio peaks before leveling off.

The ratio of carbon gasified to that combusted linearly increases with increasing  $[H_2O]_0/[O_2]_0$ . Increasing the oxygen flow rate decreases  $CO_2$  concentration in the exit gas. This is so because at higher oxygen flow rates, the comparative amount of heat loss from the gasifier to that utilized in the reduction zone of the reactor is proportionally lower than those obtained at lower oxygen flow rates. Also, increasing the oxygen flow rate leads to higher  $CO/CO_2$  and lower  $H_2/CO$  ratios.



**Fig. 2-** Effect of feed  $[H_2O]_0/[O_2]_0$  ratio on the composition of producer gas.

## 2010 Annual Report

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### 3.1 Project Impact

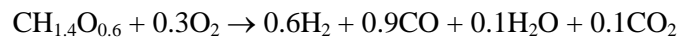
Florida imports all of its transportation fuels. The economy of Florida depends heavily on tourism and agriculture – both of which energy intensive (more appropriately, liquid fuel intensive) end-use sectors. Transportation accounts for 35% of all energy consumption in Florida, which makes it the largest energy-consuming sector of the state economy. In 2005, just the motor gasoline consumption per capita in Florida exceeded 491 gallons. According to the data compiled by the U.S. Department of Energy (DOE) Energy Information Administration (EIA), in 2006, Florida spent close to \$30B on the petroleum-based fuels – money that could have remained in the state creating jobs and improving Florida's economy.

**Production of liquid hydrocarbons from biomass is more desirable than generating oxygenated fuels such as ethanol, butanol and biodiesel made by fermentation or esterification of biomass-**

derived feedstocks. For example, the lower heating value (LHV) of ethanol (an oxygenated fuel) is 21,282 MJ/m<sup>3</sup>, which is considerably lower than that of gasoline: 32,343 MJ/m<sup>3</sup>. The higher energy content of the fuel translates to longer vehicle driving range for a given quantity of fuel onboard. Furthermore, the chemical composition and physical characteristics of synthetic hydrocarbons is essentially similar to that of petroleum-derived fuels (although less polluting), which simplifies their use in the existing engines and fuel distribution infrastructure.

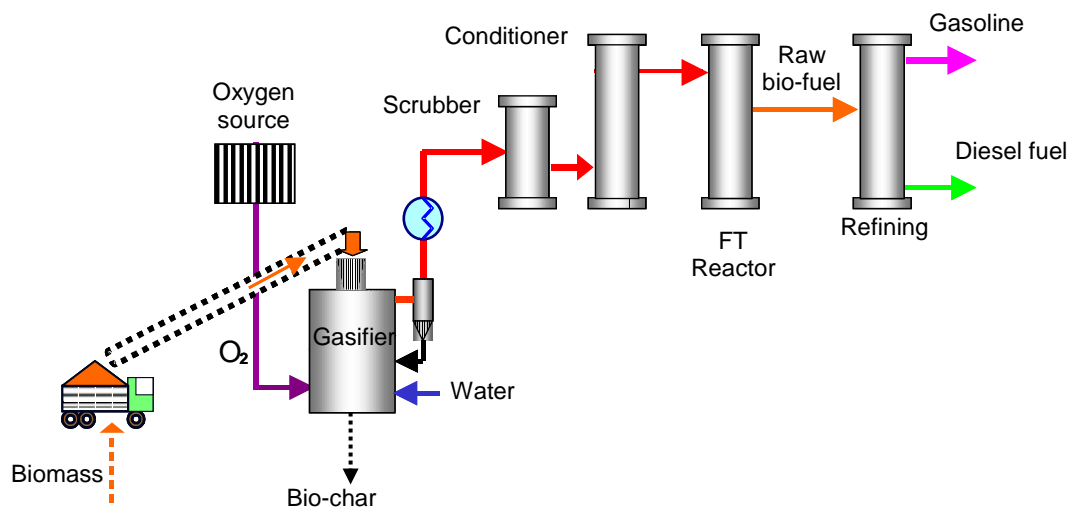
**Fig. 1** depicts a process for converting biomass to liquid fuels – gasification followed by FT synthesis. FT synthesis for indirect biomass-to-liquid fuels production offers many advantages. For example, hydrocarbon synthesis is generally non-selective process (*i.e.* governed by the so-called Schulz-Flory distribution). But, FT process has the ability to produce a range of gaseous and liquid hydrocarbons readily upgradeable thorough conventional refinery operations (*e.g.*, distillation, hydrocracking). The design of the reactor also affects the product slate. Fluidized bed reactors maximize gasoline yields, while fixed-bed reactors produce mostly diesel range hydrocarbons.

Conventional processes for thermochemical conversion of biomass to synthetic liquid fuels by air gasification have several drawbacks. For example, air gasification produces syngas that is highly diluted with nitrogen – requiring expensive nitrogen separation step downstream before it can be converted to FT hydrocarbons. The approach used here is to employ an air separation unit to generate oxygen which is then fed into the gasifier – alone or in combination with steam producing syngas according to:



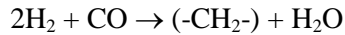
Where, CH<sub>1.4</sub>O<sub>0.6</sub> represents the empirical formula for biomass.

In the equation above, the H<sub>2</sub>/CO molar ratio for the syngas is 0.67. Depending on the biomass feedstock and operational parameters in the gasifier, a high-surface area carbonaceous byproduct (char) is also produced (thus, increasing H<sub>2</sub>/CO ratio). The char byproduct combined with activated carbon (AC) will then be used to capture N-, P-, and S-containing impurities in the raw gas exiting gasifier. The final char/AC product is enriched with the mineral compounds (N-, K-, P-based) and is then available for use as either an effective soil amending bio-char or feedstock into the carbon fuel cell.



**Fig. 1-** Bio-diesel production via integrated biomass gasification/FT process.

In the next step, the syngas enters into a FT reactor where catalytic hydrocarbon synthesis reaction takes place according to:

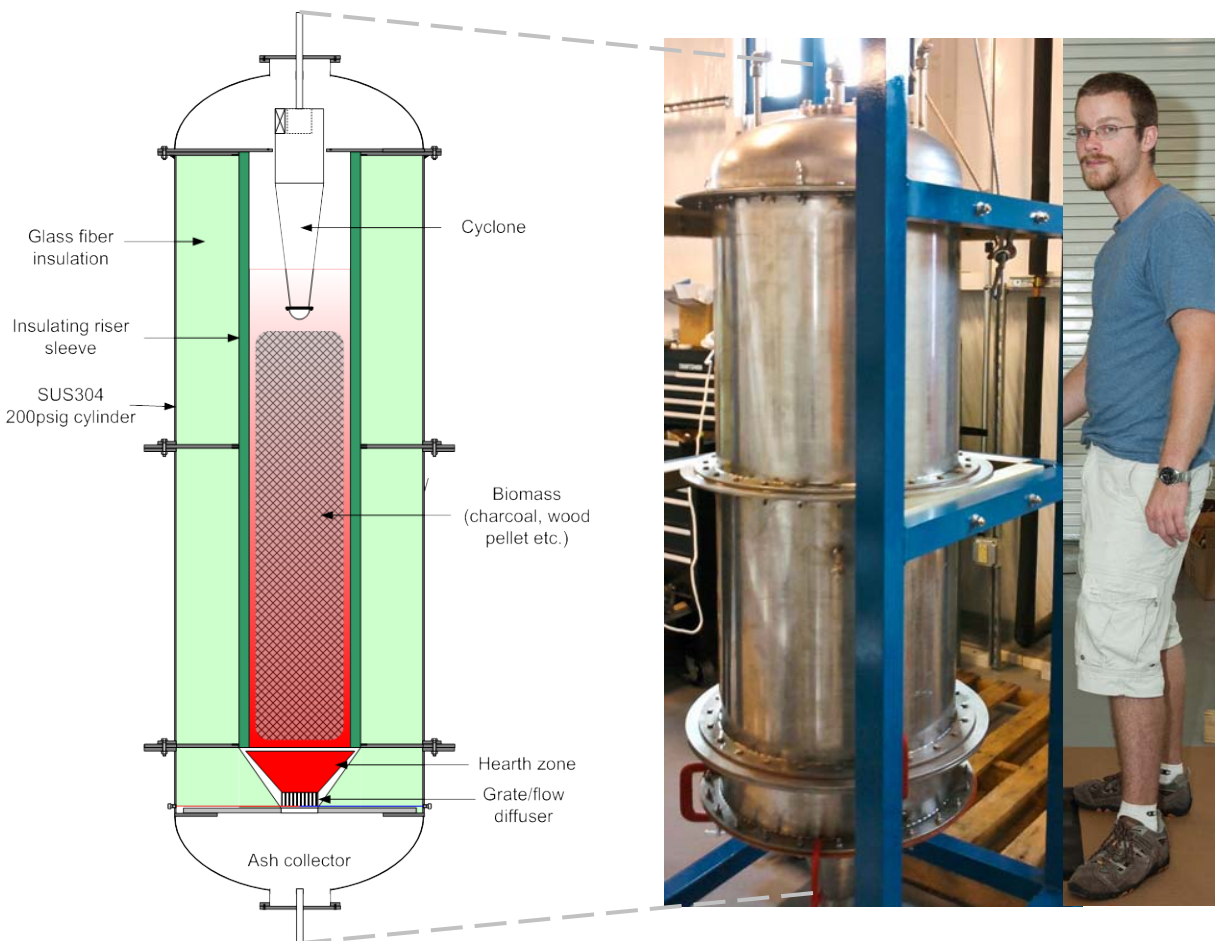


The FT synthesis reactor produces a mixture of liquid hydrocarbons (typically, C<sub>5</sub>-C<sub>35</sub>). To make the hydrocarbon mix suitable as a transportation fuel, the raw liquid product has to be processed further (*e.g.*, via distillation or hydrocracking) to gasoline (C<sub>5</sub>-C<sub>11</sub>) and/or diesel (C<sub>12</sub>-C<sub>18</sub>) fractions.

The FT catalyst development is still an area of intense research. FT-synthesized hydrocarbons have many advantages over oil-derived hydrocarbons as they do not contain sulfur, nitrogen or heavy metals, and also have low aromatic content, which results in the production of high-quality liquid fuels.

### PDU-Scale Biomass Gasification System Design and Fabrication

**Fig. 2** depicts a schematic diagram of the FSEC designed PDU-scale oxygen-blown gasifier.

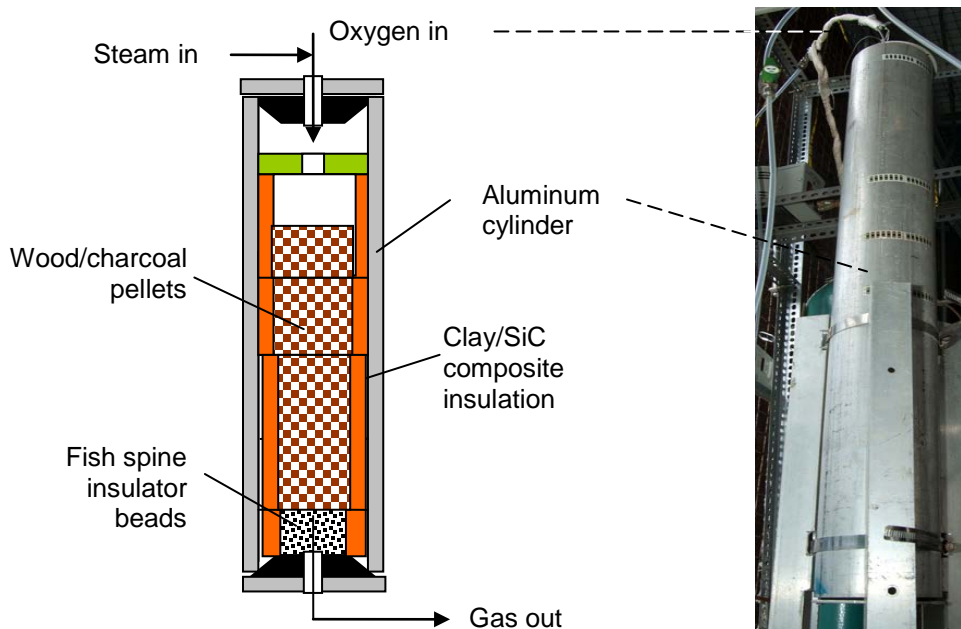


**Fig. 2-** FSEC’s PDU scale gasifier at the fab shop.

The gasifier is about 5’ in length, 17.5” ID and built with 304SS. It is designed to run under pressure (up to 200 psig) in either updraft or downdraft mode. The insulating riser sleeve holding the wood/charcoal pellets is 9” ID and the reactor hearth has an ID of 3.25”. In the updraft mode, the oxygen and steam would enter from the bottom and pass through the grate and react with the fuel in the combustion zone.

The synthesis gas produced moves up passing through a cyclone separator before exiting at the top of the gasifier.

The experimental data reported here were obtained in a small gasifier made of an aluminum tube as shown in **Fig. 3**. The idea was to collect operational data that would be useful for the design and operation of the PDU-scale gasifier. The small gasifier consists of an aluminum cylinder with an ID of 4" and OD of 4.5". The gasifier was sealed with help of two rubber stoppers with a lid screwed in to keep it in place. The gasifier was insulated with specially prepared clay/SiC composite insulating inserts which were snugly fit into the aluminum cylinder. The internal diameter of the hearth was 3". A schematic and photograph of the FSEC's small-scale gasifier is shown in **Fig. 3**.



**Fig. 3-** FSEC's small-scale gasifier.

The gasifier was run in the top-lit downdraft mode. Oxygen and water were introduced at the top of the gasifier and the producer gas exited from the bottom. The oxygen was metered with a rotameter and the water (when used as liquid) was pumped using a syringe pump. When steam was used, an electric steam generator was utilized to supply the required amount. The gas exited gasifier was cooled and the water condensed. The gas from the condenser was periodically sampled and analyzed using a Varian 450 GC.

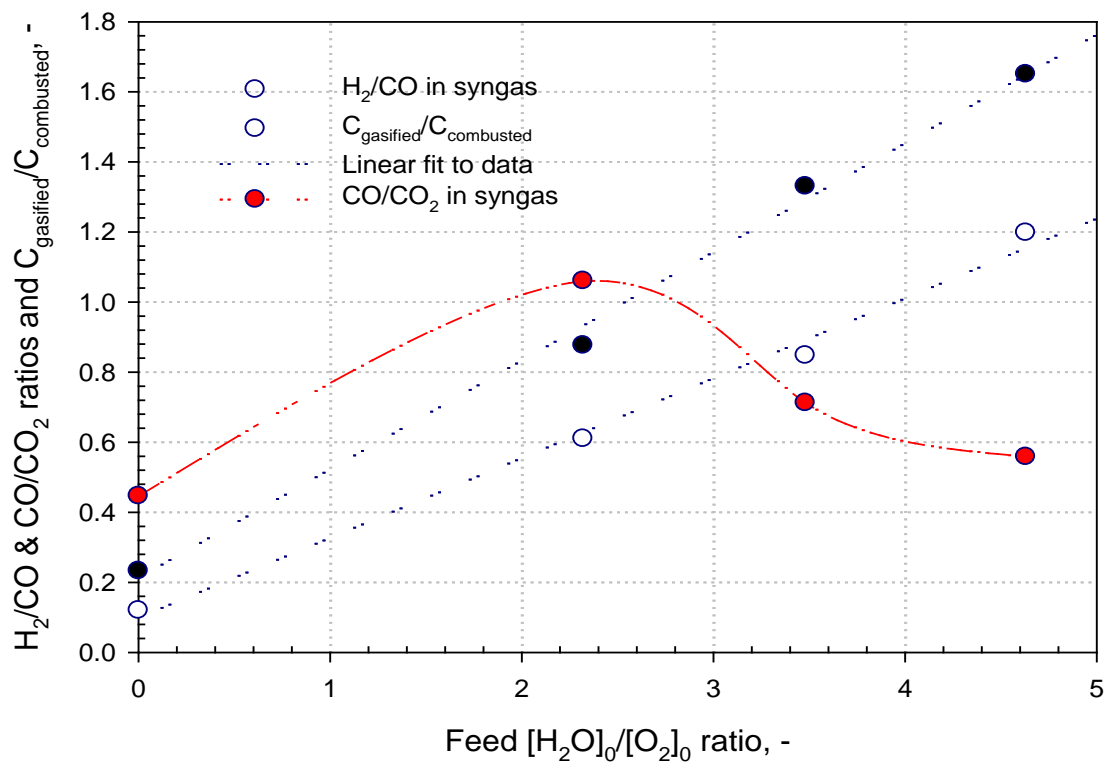
The gasifier was started by placing several glowing hot briquettes of hardwood charcoal with O<sub>2</sub> flowing into the gasifier till an even red hot combustion zone was observed. Then, the top lid of the gasifier was secured and oxygen and water flow to the reactor turned on.



## Results and Discussion

Biomass is a hydrogen deficient resource containing only about 6 wt% H<sub>2</sub>; whereas FT process typically requires an input gas composition of H<sub>2</sub>:CO=2:1 for complete utilization of the CO and H<sub>2</sub>. There are several methods to boost the hydrogen content of the producer gas. For example, a water-gas shift reactor placed after the gasifier will be able to convert some of the CO, by reacting with H<sub>2</sub>O, to hydrogen. Another way to increase the H<sub>2</sub>:CO ratio in the producer gas would be to input water with O<sub>2</sub> into the gasifier thus performing the water-gas shift reaction, in-situ. In the later case, water functions as both a combustion zone temperature moderating agent and a reactant to generate H<sub>2</sub>.

**Fig. 4** depicts how H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratio vary with input [H<sub>2</sub>O]<sub>0</sub>/[O<sub>2</sub>]<sub>0</sub> ratio. In these experiments, water was fed to the gasifier in the form of steam. The oxygen flow rate was kept constant at 5.12 g/min while the steam flow rate was varied. All the results reported here are for the brief pseudo-steady state conditions reached within the gasifier. The data of **Fig. 4** indicate that the H<sub>2</sub>/CO ratio varies linearly with the inlet [H<sub>2</sub>O]<sub>0</sub>/[O<sub>2</sub>]<sub>0</sub> ratio, while the CO/CO<sub>2</sub> ratio peaks before dropping and leveling off at somewhat higher [H<sub>2</sub>O]<sub>0</sub>/[O<sub>2</sub>]<sub>0</sub> ratios. The decrease in CO/CO<sub>2</sub> ratio at high [H<sub>2</sub>O]<sub>0</sub>/[O<sub>2</sub>]<sub>0</sub> is, in all likelihood, due to the fact that water gas shift reaction generates more CO<sub>2</sub> in expense of CO. Also, the ratio of charcoal (carbon) gasified to that combusted varies linearly with the input [H<sub>2</sub>O]<sub>0</sub>/[O<sub>2</sub>]<sub>0</sub> ratio.



**Fig. 4-** Effect of inlet [H<sub>2</sub>O]<sub>0</sub>/[O<sub>2</sub>]<sub>0</sub> molar ratio on gasification of charcoal.

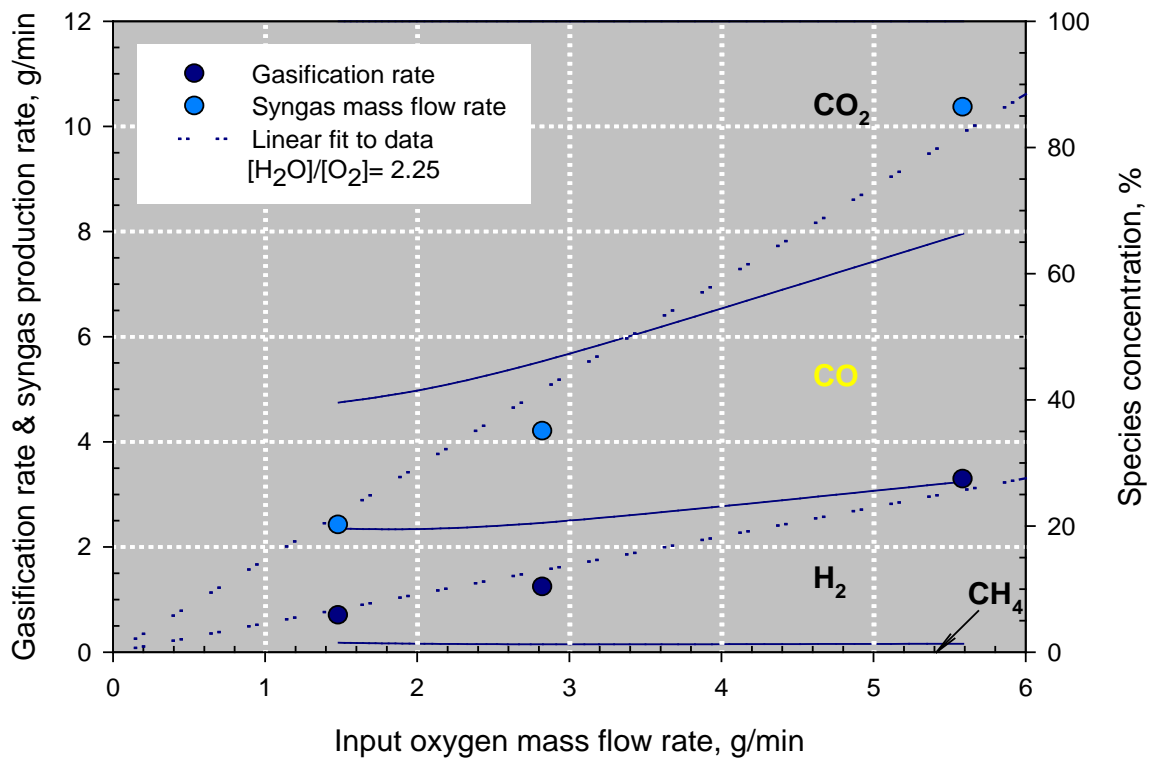
To determine the effect of latent heat of vaporization of water on gasifier performance, experiments were carried out at 5.12 g/min of O<sub>2</sub> flow while keeping the inlet [H<sub>2</sub>O]<sub>0</sub>/[O<sub>2</sub>]<sub>0</sub> ratio constant at 2.25. Results are summarized in the **Table 1** below:

**Table 1-** Physical state of input water affects the gasification rate of charcoal.

State of water	H <sub>2</sub> /CO	CO/CO <sub>2</sub>	Rate of charcoal consumption, g/min
Liquid at RT	0.65	1.17	3.28
Steam at 1 atm pressure	0.88	1.05	3.45

As expected, introducing water in the form of steam increases H<sub>2</sub>/CO ratio in the producer gas, significantly. The effect on the CO/CO<sub>2</sub> ratio is modest. The rate of charcoal consumption remains almost unaffected.

**Fig. 5** depicts the effect of increasing oxygen mass flow rate on the syngas composition and the rate of charcoal gasification. As the oxygen flow rate is increased, the CO<sub>2</sub> concentration decreases while both CO and H<sub>2</sub> concentrations increase. This can be attributed to the fact that at higher oxygen flow rates, heat loss from the gasifier is comparatively (to that utilized in the reduction zone of the reactor) less than that at lower input oxygen flow rates. This leads to an increase in the extent of the gasification reactions and hence higher rates of producer gas from the reactor. Higher oxygen flow rates are also beneficial to obtaining a more uniform combustion zone – thus reducing bypassing of the CO<sub>2</sub> through colder regions.



**Fig. 5-** Effect of increasing oxygen mass flow rate.

### Conclusions

The following conclusions can be drawn from the experimental data presented above:

The ratio of H<sub>2</sub>/CO in the producer gas can be increased by increasing the inlet [H<sub>2</sub>O]<sub>0</sub>/[O<sub>2</sub>]<sub>0</sub> ratio.

Increasing the input oxygen flow rate to the gasifier results in a decrease in CO<sub>2</sub> concentration in the exit gas. This is due to the establishment of a more uniform combustion zone at high oxygen flow rates and subsequent reduction in the heat loss from the gasifier.