

Thrust Area 3: Biomass (Thermo-Chemical Conversion) *Integrated Florida Bio-Energy Industry*

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Description: The aim of this project is to produce liquid hydrocarbon fuels (LHF) derived from Florida's biomass resources utilizing a two-step thermochemical process. In the first step, biomass is gasified with oxygen and steam to synthesis gas (syngas) comprised of mostly hydrogen and carbon monoxide. Use of oxygen for gasification of biomass allows higher overall process energy conversion efficiency to be realized as it circumvents syngas dilution with nitrogen (if air is used instead). In the second step, syngas is cleaned and then fed into a Fischer Tropsch synthesis unit that converts the synthesis gas to liquid hydrocarbon fuels containing gasoline and diesel fractions. 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: \$386,409

Universities: UCF-FSEC

Progress Summary

The aim of this project is to produce liquid hydrocarbon fuels (LHF) derived from Florida's biomass resources utilizing a two-step thermochemical process. The first step of the process comprised of a pilot-scale gasifier that was operated using pinewood charcoal as the feedstock. The gasifier operated in bottom-lit updraft mode using a mixture of oxygen and steam as oxidizing agents - introduced from the bottom of the gasifier, and the output gas exited from the top (see picture below). The main objective of the gasification experiments was to determine the effect of oxidant flow rate and inlet $[H_2O]_0/[O_2]_0$ ratio on the performance of the gasifier and quality and composition of the syngas produced.

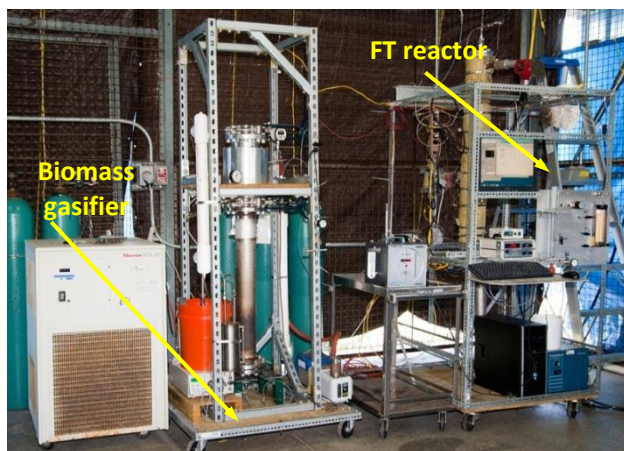


Table below presents typical experimental data collected during one integrated gasifier-Fischer Tropsch (FT) synthesis run in which the gasifier pressure was set at 100 psig and flow rates of oxygen and water were 2700 mL/min and 270 g/hr, respectively. The gasifier biomass feed consisted of a mixture of about 800g of pinewood charcoal and 131.6g of virgin pinewood pellets.

Time, min	Thru FT reactor?	%CO	%H ₂	%CO ₂	%CH ₄	Syngas flow rate, L/min
9	NO	43.3	32.8	21.9	1.8	8.92
32	NO	40.0	28.9	25.9	5.35	9.78
46	NO	34.5	30.9	27.9	5.56	9.21
80	YES	31.0	31.8	29.6	5.60	9.16
110	YES	35.0	33.6	26.1	5.04	9.06
136	YES	38.4	29.7	24.0	6.25	8.42
155	NO	38.3	30.9	24.7	5.85	9.00
175	YES	42.6	33.0	20.1	3.32	8.30
180	YES	44.0	32.2	20.5	2.98	5.94

The second step of the process comprised of a FT reactor that was operated at 240°C temperature. A slipstream of about 1.5 L/min was diverted from the gasifier exit line and passed through the FT reactor. At the end of the run, approximately 0.53g of organic liquid product was collected. The GC-FID analysis of the condensate showed that it composed of about 33.13 wt% gasoline range (C₅-C₁₀), 7.52 wt% kerosene/jet fuel range (C₁₁-C₁₂), 23.22 wt% diesel range (C₁₃-C₁₆), and 36.14 wt% lube oil and wax range (C₁₇-C₂₆) hydrocarbons.

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Background: The growing demand for clean renewable energy is creating market pull worldwide to develop viable environmentally benign processes for converting biomass to liquid hydrocarbon fuels (LHF). The objective of this project was to develop a viable thermochemical process for converting Florida-grown biomass to fungible liquid transportation fuels. Biomass feedstocks selected for this investigation included both lignocellulosic (*e.g.* pinewood) and aquatic (*e.g.* duckweed) species. The approach taken for processing the biomass-to-liquid fuels (BTL) involved two successive steps – 1) syngas (a mixed gas comprised of mostly hydrogen and carbon monoxide) production via gasification of biomass with steam and oxygen; 2) syngas to LHF conversion via Fischer-Tropsch (FT) synthesis. A more detailed description of the BTL process is given below.

Integrated biomass gasification and Fischer-Tropsch synthesis: Gasification coupled with Fischer-Tropsch (FT) synthesis offers many advantages. For one, any source of biomass can be used in the process (*e.g.*, lignocellulosic materials such as crop residues, forest waste, yard clippings, energy crops; as well as the aquatic biomass. For another, the process generates a range of liquid hydrocarbons that can be easily upgraded to fungible transportation fuels (*e.g.*, gasoline, diesel, aviation fuels, etc.) using conventional refining operations such as distillation, hydrocracking, etc.

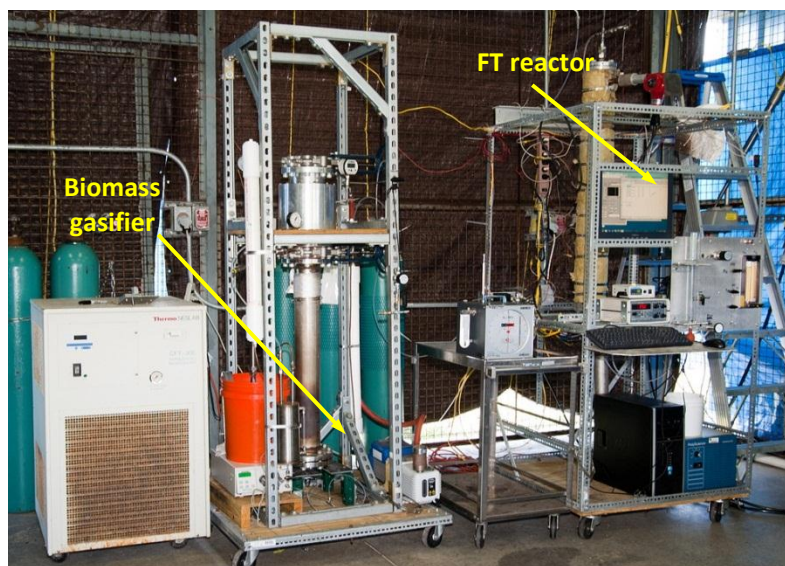
This is a two-step process. In the first step, biomass is gasified with oxygen and steam to synthesis gas (syngas) comprised of mostly hydrogen and carbon monoxide. Use of oxygen for gasification of biomass allows higher overall process energy conversion efficiency to be realized as it circumvents syngas dilution with nitrogen (if air is used instead). In the second step, syngas is cleaned and then fed into a FT synthesis unit that converts the synthesis gas to LHF containing gasoline and diesel fractions.

The biomass gasification experiments employed several different gasifiers – all designed, fabricated and tested at the Florida Solar Energy Center (FSEC). In order to identify the best gasification configuration, operational parameters (*e.g.*, temperature, pressure, steam/oxygen ratio, rate of biomass gasification, etc.) for each reactor design were varied and their effect on the amount and composition of syngas (especially H₂/CO ratio), and the extent of CO₂ generated were determined. It was found that the H₂/CO ratio and the rate of biomass gasification increase monotonically as a function of [H₂O]/[O₂] ratio (at a fixed O₂ flow rate). Also, there appeared to be an optimum [H₂O]/[O₂] ratio for which the CO₂ concentration in the syngas was minimum.

The FT synthesis of liquid hydrocarbon fuels was conducted in a number of fixed-bed reactor designs. FT reactors used especially prepared (at FSEC) catalysts including, among others: K-promoted and silica-supported iron, silica-supported cobalt, molybdenum-Zeolite Y. It was found that Fe-based catalysts produced LHF (mainly, C₅-C₂₂ hydrocarbons) rich in unsaturated hydrocarbons. The unsaturated hydrocarbons tend to adversely affect the long-term stability of the fuel.

Unlike iron-based catalysts, the cobalt-based catalysts produce mostly straight chain alkanes that remain stable for much longer period of time. Catalyst combinations such as Fe+Ni-Mo/alumina, Fe+H⁺-ZSM-5 were also evaluated for their potential to improve the quality of LHF produced. Also, issues related to heat and mass transfer in the FT reactors were investigated. Finally, a new FT reactor design having radial flow configuration was built and tested showing improved heat and mass transfer characteristics.

A fully integrated and instrumented (using Lab-View platform) pilot-scale BTL system was built and tested. The unit operates continuously and is comprised of an oxygen-blown gasifier, a cyclone separator, syngas purification and conditioning unit, a steam generator, an FT synthesis reactor, and a product collection system. The integrated system employed a bottom-lit updraft gasifier, and an FT radial flow reactor loaded with silica-supported cobalt (Co/silica) catalyst. The liquid product collected after a typical run consisted of a hydrocarbon fraction, mainly, C₆-C₂₄ saturated hydrocarbons and excess water. Also, the integrated unit did produce a small amount of higher molecular weight waxy hydrocarbon compound (see picture below).



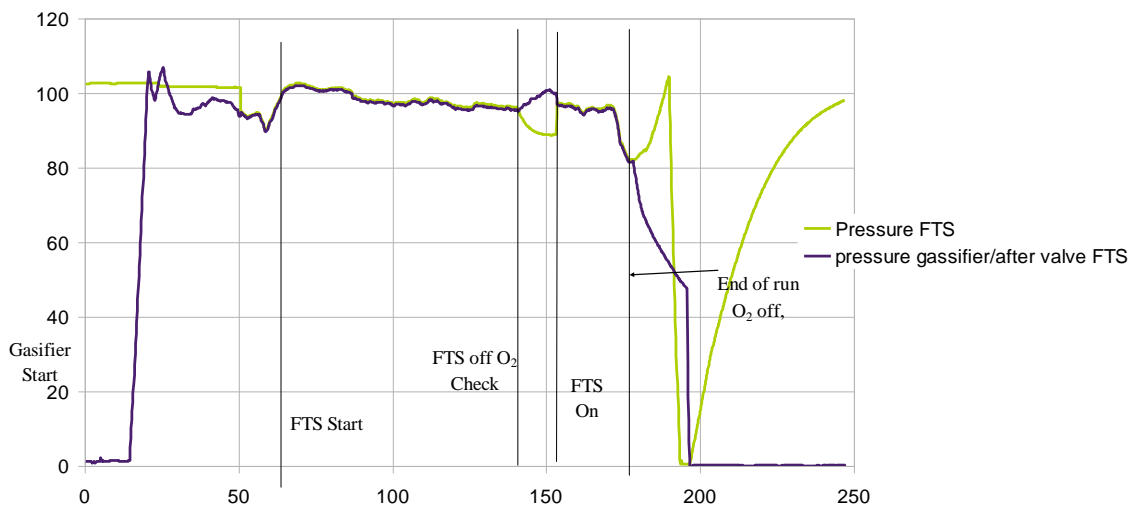
Results and Discussion: In a typical run, the integrated gasifier-Fischer Tropsch (FT) synthesis reactor operated at a system pressure of 100 psig. The flow rates of oxygen and water entering the gasifier were 2700 mL/min and 270 g/hr, respectively. The biomass was fed continuously to the gasifier and consisted of about 800g of pinewood charcoal mixed with 131.6g of virgin pinewood pellets. The data obtained are shown below.

Run time, min	Thru FT reactor?	%CO	%H ₂	%CO ₂	%CH ₄	Syngas flow rate, L/min
9	NO	43.3	32.8	21.9	1.8	8.92
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136	YES	38.4	29.7	24.0	6.25	8.42
155	NO	38.3	30.9	24.7	5.85	9.00
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The first entry to the table (at 9 min) was at atmospheric pressure and the rest were at 100 psig. The run was terminated at 180 min through since the output gas flow rate (as well as pressure) began to drop indicating that the fuel was exhausted. The profile of gasifier internal pressure is shown below.

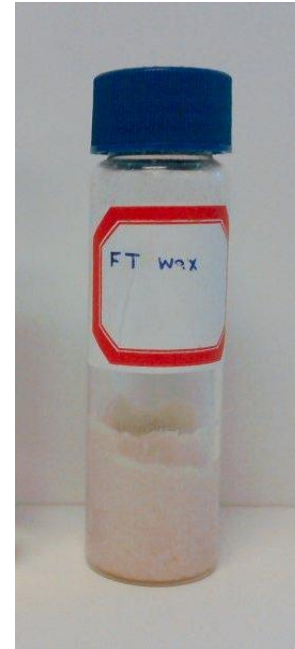
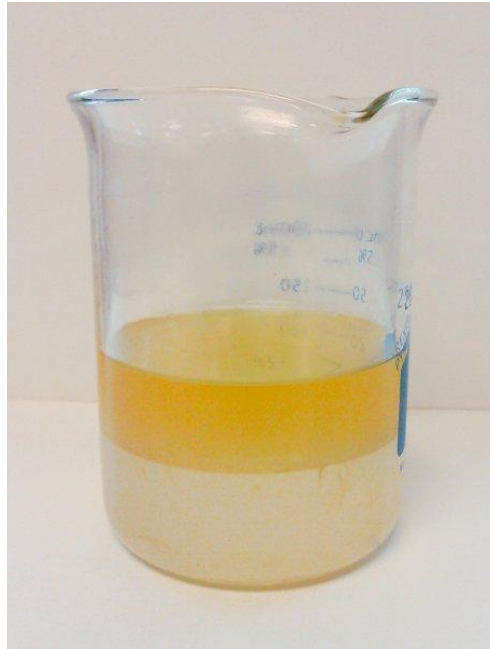
The second step in the process involves Fischer-Tropsch (FT) treatment of the syngas generated by the gasifier. The FT reactor operated at 240°C temperature. A slipstream of about 1.5 L/min was diverted from the gasifier exit line and passed through the FT reactor. At the end of the experiment, approximately 0.53g of organic liquid product was collected.

The GC-FID analysis of the condensate showed that it composed of about 33.13 wt% gasoline range (C₅-C₁₀), 7.52 wt% kerosene/jet fuel range (C₁₁-C₁₂), 23.22 wt% diesel range (C₁₃-C₁₆), and 36.14 wt% lube oil and wax range (C₁₇-C₂₆) hydrocarbons.



Thus, we were able to demonstrate production of LHF (especially, gasoline and diesel range synthetic hydrocarbon fuels) directly from biomass derived syngas. The following Figure depicts the

raw products of Fischer-Tropsch synthesis of pinewood derived syngas obtained during the operation of the pilot scale unit. The upper layer on the left photo is hydrocarbons, and the lower layer – water. Right Photo shows waxy product obtained during FT reaction.



Large-Scale BTL Plant Design, Modeling and Costing: Based on the extensive experimental data collected, and using the AspenPlus™ chemical process simulation platform, a preliminary flowsheet of a full-scale biomass-to-liquid fuel plant was prepared and its economics evaluated. The Aspen generated output for a single set of non-optimized operating conditions was used to conduct order-of-magnitude estimates of the total plant cost and from that, the fully burdened cost of the fuel generated. Table below depicts the assumptions used for the cost analysis.

Process		Capital Costs	
Design capacity (kg FT fuel produced/yr)	93,688,930	Total direct & indirect depreciable (2005\$)	310,850,202
Capacity factor	0.90	Total non-depreciable (2005 \$)	250,000
Actual FT fuel production (kg/yr)	84,320,037	Total Capital Investment (TCI) (2005 \$)	311,050,000
Financial		Annual Operating Costs	
Start-up year	2025	Total plant staff	50
Analysis period (yrs)	15	\$/man-hr (including overhead)	50
Plant life (yrs)	25	Prop tax & insurance rate (% TCI)	2
Depreciation type	MACRS	Maintenance (% dir cap cost)	0.50
Depreciation period (yrs)	20	Waste treatment & disposal (%TCI)	1.0
% Equity financing	100	Other raw material costs (catalyst, boiler chem., cooling tower chem.) \$/yr	5,000,000
Decommissioning costs (% deprec capital)	10	Biomass feed, \$/ton	163
Salvage value (% total capital)	10	Electricity (credit) \$/kWh	0.056
Inflation rate (%)	1.90		
After tax Real IRR (%)	10		
Total tax rate (%)	38.9		

Based on this analysis, the integrated biomass gasification and FT synthesis process is thermodynamically and economically feasible with an overall efficiency of about 40% based on polygeneration of fuel, heat and power. Simulation results indicate that the biomass feedstock costs make up about 54.4% of the total cost of liquid fuel produced. At biomass cost of \$163/ton and plant production capacity of 84,320 metric ton per year, the cost of LHF would be about \$7 per gallon. If lower cost biomass feedstocks are available, a fuel cost in the range of \$3/gallon can be realized; as shown in the Table below.

Cost component	Cost (\$/kg of FT fuel produced)	% of total cost
Capital costs	0.81	39.3
Fixed O & M	0.18	8.6
Feedstock	1.12	54.4
Other raw materials	0.06	3.0
Byproduct credits - electricity generation	-0.13	-6.5
Other variable costs	0.02	1.2
Synfuel cost (at the gate)	\$2.06	Per kg
	\$7.00	Per gallon



Nazim Muradov, Principal Research Scientist at the Florida Solar Energy Center, shows Florida Agriculture Commissioner Adam Putnam, biomass that can be made into diesel fuel.

Photo credit: Malcolm Denmark, FLORIDA TODAY

Acknowledgements: Funding for this project was provided by a grant from the Florida Department of Agriculture & Consumer Services (FL DACS) – Farm-to-Fuel program. Additional funds were made available by the UCF-FSEC and with indirect support (matching funds) of the Florida Hydrogen Initiative (FHI), Chevron Technology Ventures (CTV) and Florida Energy Systems Consortium (FESC). We thank Dr. Bill Grieco of the PetroAlgae, Inc. for providing duckweed samples used in some of the pyrolysis and gasification experiments reported here. We are also grateful to the both past and present (see picture below) Florida Agriculture Commissioners and especially to Mr. Jay Levenstein, Deputy Commissioner at the Florida Department of Agriculture & Consumer Services.