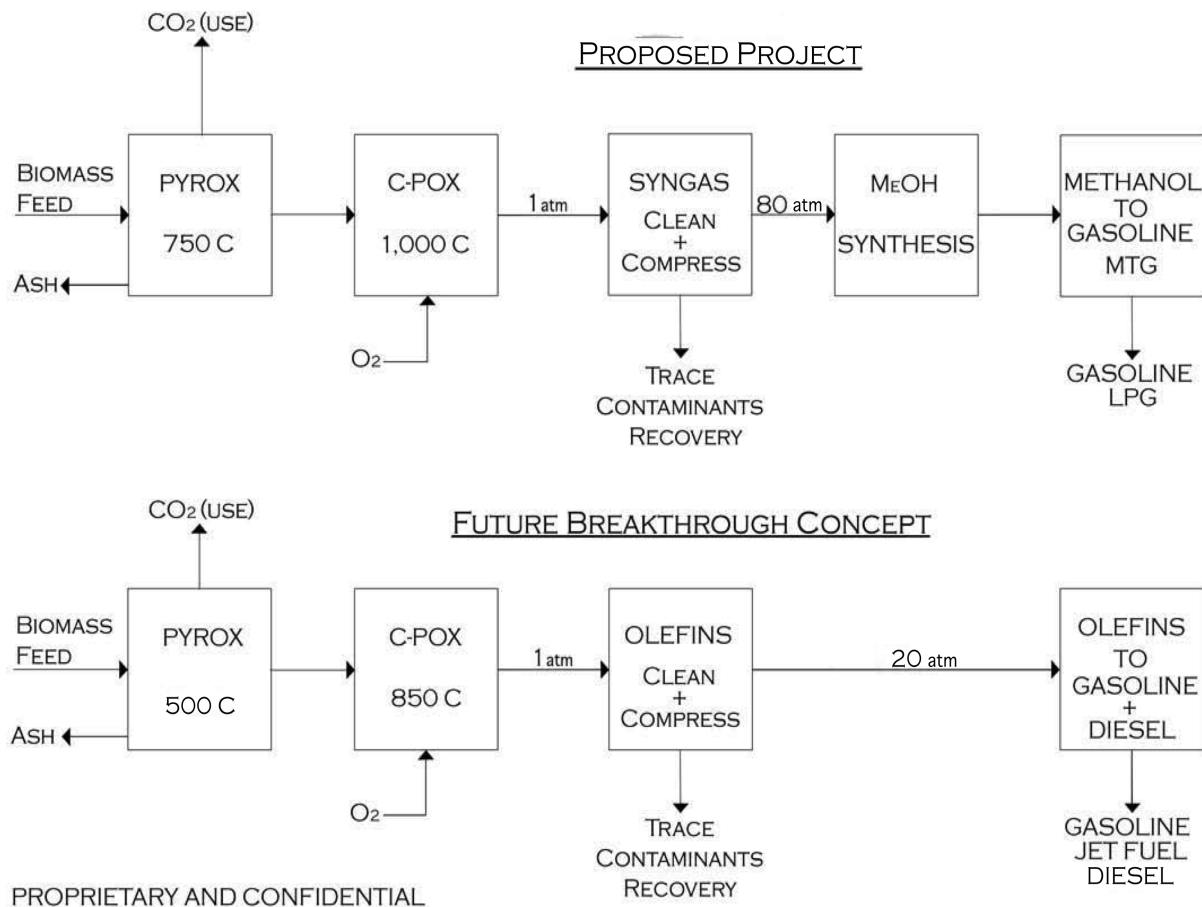


## 1.0 Break-Through Process Proposed for EISG funding

The proposing team, working with Exxon executives, has preformed preliminary economic and technical evaluations focusing on the existing state-of-the-art pathway for “medium-scale” conversion of biomass-to-gasoline (2000 barrel per day scale), using **methanol** as the chemical intermediate (MTG, methanol-to-gasoline technology), which is shown below:



The break-through path, shown above, uses **light-olefins** as the chemical intermediate, instead of methanol. A liquid synthesis route using light-olefins offers capital cost reduction benefits when compared to using the syngas-to-methanol approach, which path serves as the bench-mark for the best available thermal chemical path available today. The proof-of-concept project will prove the breakthrough pathway shown above; however, focusing only on the conversion of biomass to light olefins using a two stage process.

Production of high-quality light-olefins using a fluid-bed process that is close-coupled to a secondary catalytic reactor requires proof-of-concept testing and technical development, which will be accomplished by operating a Process Development Unit (PDU) located at CE-CERT during a 6-month test period that is proposed for funding by EISG.

It should be noted that the conversion of Refuse Derived Biomass (RDB) into pyrolysis vapors (tar vapors), followed by very rapid thermo-catalytic conversion to light-olefins was demonstrated and patented by NREL researches during the early 1990s; however, the NREL team only perform 2-days of operational

testing, which provided some “hints” about this pathway; the promising results were enough for NREL to file a general patent on the subject; but that technology path was never pursued, primarily because NREL did not have the charter to develop “refinery products” at that time. The NREL patent, issued to Ralph Overend and John Scahill, expired recently, thereby opening the door to a novel technology path with unencumbered intellectual property rights that are now in public domain.

Further evidence for the viability of this path is provided by the fact that ethylene and propylene producers, particularly including the giants on olefin production, ExxonMobile and Lummis, have recently developed and patented tar-cracking catalysts that convert petroleum tars into light-olefins. However, biomass derived tar-vapors, known as pyrolysis vapors, are even more well suited for production of light olefins, because they are high unsaturated -- and bio-tar vapors are more highly reactive compared to petroleum tars because of the extensive oxygen content.

Catalytic oxy-dehydrogenation is the method that Exxon is apparently pursuing (according to recent patents) to convert refinery tars into unsaturated gases, with the goal of producing more propylene than ethylene; oxygen is reacted with petroleum tar-vapors in the 600 – 800 C range for less than 1-second, typically less than 0.3 seconds.

**[Dr. Park, is catalytic hydro-deoxygenation is another possible path to light-olefins worth considering?]**

The existing Process Development Unit located at CE-CERT, designed and constructed by Taylor Energy, will be used to evaluate the novel CPOX technology concept that is intended to crack and reform pyrolysate oil-vapors directly into light-olefins with >40% conversion into ethylene, propylene, and butylenes.

Major Co-products include methane and carbon monoxide.

This pathway is very promising, but requires the specification of operating parameters; the data generated by NREL in 1990 shows that RDF is especially attractive as a feedstock for light-olefins because the plastics content in RDF converts directly to light-olefins. Significantly, the plastics content in RDF has increased from about 8-wt% in 1990 to about 15-wt% in 2014.

During the short two tests performed by NREL, the operating parameters were not specified using the commercial catalysts available at that time, and especially considering that new metal-oxide catalysts have been developed since then that are said to operate 100 C lower than the traditional steam cracking catalyst used during the 1990's.

## **1.1 Syngas versus Light-Olefins**

Similar thermal processing hardware that is typically used for production of synthesis gas via CPOX can also be used for olefins production. Syngas production required retention of 1-3 seconds, while olefins production requires a retention of less than 1-second. By testing the new class of petroleum refining catalysts used to reform tars into olefins it is likely that an equilibrium catalyst can be selected that is both selective and stable.

Good-quality-data resulting from biomass pyrolysis vapor conversion is not available at this time, but the technology is ready for pre-development testing proposed herein as Period-I, in preparation for development and demonstration. However, the data presented below shows the results when using an equilibrium catalyst applied to heavy petroleum feedstocks, initially for syngas production, secondarily for light-olefins.

## 1.2 CPOX--Catalyst for Syngas Production also used for Light-Olefins Formation

A major catalyst R&D Company tested a large number of catalysts; all the conceivable reforming types, including various kinds of refractory materials for steam reforming of heavy hydrocarbons. Through their experiments, they found that catalysts T-12, containing silica-free-alumina and alkaline-earth-metal-oxides was highly effective in steam reforming of heavy hydrocarbons, and caused no carbon deposition under the given conditions. Table 1 lists some of the physical properties of T-12.

**Table 1. Catalyst tested for production of Syngas and/or Light Olefins.**

ITEM	FEATURE
Form	Cylinder, Raschig rings
Crushing Strength (kg - wt/cm <sup>2</sup> )	200 - 400
Water Absorption capacity (vol %)	50
Apparent Specific Weight (gm/cm <sup>3</sup> )	4
Bulk Density (gm/cm <sup>3</sup> )	1.3
Main Chemical Constituents of Crystalline Part of catalyst	Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> and Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>

Chemical analysis of T-12 indicates that it consists mainly of CaO and Al<sub>2</sub>O<sub>3</sub> and virtually no SiO<sub>2</sub>. The effectiveness of T-12 was confirmed for syngas production using Kuwait crude oil, Bunker C, and Vacuum Residue, as shown in Table 2 below.

**Table 2. Syngas Production, using contact times of 1.14 - 1.96 sec @ 1000 C.**

Catalyst	T - 12						
	Kuwait Crude		Bunker C		Vacuum Residue		
Pressure (kg wt/cm <sup>2</sup> gauge)	0	9	0	9	0	9	
Temperature (°C)	1000	1000	1000	1000	1000	1000	
Feed Rate (kg/hr)	0.52	0.59	0.6	0.6	0.59	0.62	
H <sub>2</sub> O/C mol.	4.1	3.7	4.0	4.1	4.2	3.9	
Composition	H <sub>2</sub>	63.8	65.1	62.1	61.2	60.7	60.6
	CO	10.0	10.7	9.5	9.4	10.4	10.4
	CO <sub>2</sub>	16.1	15.3	16.0	16.5	19.8	16.4
	CH <sub>4</sub>	9.0	8.9	9.1	11.1	8.0	9.1
	C <sub>2</sub> H <sub>4</sub>	-	-	-	-	0.9	0.02

Pressure looks to have little effects on the composition of the product gas. Based on the results above, the basic structure of a reformer was determined for pilot testing and the standard operating conditions suggested were around 1050 C with steam/carbon ration of 3 - 4 for continuous operation.

### **1.3 Pilot-plant results from Thermal Reforming Process**

After successful completion of the above bench-scale test, a module-type pilot plant was constructed at the catalyst development company. Table 3 lists data from the plant, as well as another pilot-plant of larger size. It should be kept in mind here, operating conditions in Table 3 were optimized to produce olefins at high conversion rate; this means that T-12 is useful for H<sub>2</sub>/CO production in the higher temperature range, and also useful for olefins production at lower temperature and shorter retention time.

There are questions remaining, of course, about the amount of the oxygen consumption required, the retention time, (which is very short compared to syngas formation), the optimum temperature, the amount of superheated-steam needed for dilution, and the optimum catalyst type needed for long-life and low-cost. Proof-of-concept testing, using the Process Development Unit at CE-CERT, will establish these parameters with greater precision for the path to light-olefins using CPOX as the methodology.

### **1.4 Olefins formation with CPOX**

Production of light-olefins is somewhat more difficult to accomplish compared to syngas formation. The kinetics are very quick and the reactor-retention-times are very short (only fractions of a second). Moreover, conversion of biomass-to-olefins will not be 100% efficient; for example, CH<sub>4</sub> and CO are significant co-products formed during olefins formation, and therefore, one must consider various bottoming cycles that recover CH<sub>4</sub> and use CO-rich syngas.

At small scale, purge-gases would likely be used for on-site power generation needs. At larger scale, bio-methane would be recovered as a co-product. The research goal of the proposed proof-of-concept project is to achieve >40% conversion to light-olefins. In the scenario proposed, light-olefins would be used as a collective feed for the “olefins to gasoline & diesel” process that was demonstrated by ExxonMobile at 70 bbl/day scale, but not commercialized. The principal investigator was informed confidentially by Exxon executives that there is “interest” within Exxon Research to participate in developing olefins-to-aviation fuel; and that there is a particularly “strong interest” in employing Refuse Derived Biomass as the feed.

Process optimization would be accomplished during a subsequent Period-2, Research & Development. Additional engineering is required to select the optimum back-end synthesis methodology to utilize Olefins to Gasoline & Diesel. The issues to be resolved by detailed engineering (during a Period-2) relate primarily to estimating the capital costs along with process simplifications intended to improve economic performance.

**Table 3. Light-Olefins production contact times of 0.015 - 0.68 sec @ 820-850 C.**

Catalyst	T - 12							
Run No.	389		206		226		322	
Feed Oil	naphta		kerosene		light gas oil		vacuum gas oil	
Temperature (°C)	850		820		831		840	
Pressure (kg wt/cm <sup>2</sup> gauge)	0.0		0.0		0.0		0.0	
Contact Time ( sec)	0.68		0.2		0.169		0.015	
Steam/Carbon (mol)	1.02		1.17		0.54		0.59	
Gasification (wt %)	80.1		76.6		69.6		56.9	
Products	Composition		Composition		Composition		Composition	
	vol %	wt %	vol %	wt %	vol %	wt %	vol %	wt %
H <sub>2</sub>	26.4	2.5	32.2	3.0	30.2	2.4	14.9	0.8
CO	1.9	2.5	2.8	9.6	0.8	0.9	0.4	0.3
CO <sub>2</sub>	6.7	13.8	9.8	19.7	9.7	16.7	1.0	1.1
CH <sub>4</sub>	23.1	17.3	18.8	13.8	16.5	10.4	21.3	8.8
C <sub>2</sub> H <sub>6</sub>	1.3	1.8	1.4	1.9	2.0	2.4	2.7	2.1
C <sub>2</sub> H <sub>4</sub>	27.7	36.3	23.3	29.8	23.3	25.6	31.8	23.0
C <sub>3</sub> H <sub>8</sub>	0.4	0.9	0.2	0.4	0.3	0.5	0.6	0.7
C <sub>3</sub> H <sub>6</sub>	6.8	13.4	8.0	15.4	10.0	16.5	13.2	14.3
C <sub>4</sub> H <sub>10</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C <sub>4</sub> H <sub>8</sub>	0.4	1.0	1.3	3.3	2.0	4.4	1.7	2.4
C <sub>4</sub> H <sub>6</sub>	1.9	4.8	2.4	6.0	2.6	5.4	4.7	6.6