# Technical and Economic Feasibility of Mixed Alcohols Fuel Production from Biomass-derived Syngas

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## Introduction

This research was conducted to investigate possible thermochemical routes (as opposed to biochemical) for producing ethanol. A stand-alone mixed alcohols process was the basis for this modeling work. The technoeconomic models developed for biomass gasification and subsequent mixed alcohols synthesis will further be used in FY06 to create an integrated biochemical/thermochemical biorefinery model capable of quantifying the benefits of combining the two technology platforms.

There is an exhaustive amount of literature and data available on "gas-to-liquids" (GTL) technology capable of producing fuels and chemical products from syngas (primarily CO and $H_2$). In December 2003, NREL published the results of a preliminary screening exercise that reviewed the many syngas conversion processes and summarized the salient points regarding technology status, chemistry, process equipment choices, gas cleanliness requirements and even economics (Spath, 2003). Of the products examined in this report, hydrogen and methanol were concluded to be the best products to pursue from biomass gasification. It also stated that more analysis should be performed on mixed alcohols synthesis, in part because it was one of the few conversion technologies that had yet to be demonstrated at commercial scale.

To complete this milestone, NREL began with an extensive literature search on mixed alcohols research and technology. An engineering firm (Nexant) was also subcontracted to document the current state of mixed alcohols technology for NREL (Nexant, 2005). From this, several conceptual process designs and simulations were developed in order to generate detailed mass and energy balance data. NREL's thermochemical design report (Spath, et.al. 2005), which documented the conceptual design, detailed modeling, and economics for a stand-alone biomass gasification process for producing hydrogen ($H_2$), served as the basis for the front-end sections for the mixed alcohols process model. Mixed alcohol synthesis, separations, and purification sections were then added to the model. Model output was then used within a discounted cash flow economic analysis (DCFROR). Capital and operating costs were calculated, as well as the minimum product selling price required to meet a 10% internal rate of return (IRR). Sensitivity analyses were conducted around several parameters to determine the extent of their overall economic impact on the process.

As was done for the thermochemical design report, two process designs were completed. The current case design attempts to define today's state of technology, especially with regards to tar reformer performance. The other design, the goal case design, is a target design meant to show the effect of meeting specific research goals in tar reforming. Table 1 shows the differences in conversion between the current and goal cases. Keep in mind that for this mixed alcohols work, the goal case does not reflect any improvement in mixed alcohol technology. Potential improvements in this area of the process are quantified through sensitivity analyses.

## Table 1. Current and Goal Design Performance of Tar Reformer

| Compound | Current Case % Conversion to CO & H2 | 2010 Tar Reforming Goal Case % Conversion to CO & H2 |
|---|---|---|
| Methane ($CH_4$) | 20% | 80% |
| Ethane ($C_2H_6$) | 90% | 99% |
| Ethylene ($C_2H_4$) | 50% | 90% |
| Tars ($C_{10+}$) | 95% | 99.9% |
| Benzene ($C_6H_6$) | 70% | 99% |
| Ammonia ($NH_3$)* | 70% | 90% |

* Converts to $N_2$ and $H_2$

## Background

A literature search was conducted to review existing and prior mixed alcohol technology and how it has developed over the past 25 years. Nearly 50 literature sources were gathered and analyzed. The full list of literature reviewed is not shown in this abstract. Some of the literature contains detailed information regarding catalyst synthesis and characterization (e.g. x-ray diffraction); however, this information is not captured in this abstract because the focus was geared more towards experimental conditions and performance.

Within this abstract, the term “mixed alcohols” refers to a mixture of C1 – C6 alcohols, with preference towards the higher alcohols (C2-C6). Mixed alcohols catalysts are typically categorized into several groups based on their composition and/or derivation. Common to all of these catalysts is the addition of alkali metals which shifts the product slate towards alcohol production. Spath, et.al. 2003 categorized the catalysts into five groupings based on the work of Herman (Herman, 1991): 1) Modified high pressure methanol catalysts; 2) Modified low pressure methanol catalysts; 3) Modified Fischer-Tropsch (FT) catalysts; 4) Alkali-doped sulfides (modified methanation); 5) Other which includes alternate catalysts, such as Rhodium based catalysts, that are not specifically used for mixed alcohols but have been developed for more selective alcohols synthesis.

Others (Smith, et.al 1992). (Forzatti, et.al. 1991) group them simply into three categories: A) modified methanol catalysts, B) modified Fischer-Tropsch catalysts, and C) others. This helps to eliminate confusion that can arise when, for example, molybdenum-based sulfide catalysts are promoted with cobalt or other similar FT elements, thus representing both alkali-doped sulfides and modified-FT groupings. This 3-category system will be used in this abstract to describe the catalysts.

Since the 1920's scientists have known how to produce mixtures of methanol and other alcohols by reacting syngas over certain catalysts. They observed that when methanol catalysts (Zinc or Copper based) were promoted with an alkali, and certain reaction conditions were met (temperature, pressure) a mixture of methanol and higher alcohols resulted. At the same time, Fischer and Tropsch observed that hydrocarbon synthesis catalysts produced linear alcohols as byproducts. From this they were able to develop the "Synthol" process for producing higher alcohols. Some development continued, but it wasn't until the 1970's oil embargo that significant interest re-appeared, and researchers renewed efforts to produce higher alcohols for liquid fuels applications. As petroleum prices dropped research declined until the mid-to-late 80's when interest was driven by environmental aspects, specifically oxygenated fuel and octane enhancement.

In 1990, the Clean Air Act mandated the seasonal use of oxygenated compounds in gasoline in specific regions of the U.S. Soon after, methyl-tertiary-butyl ether (MTBE) became the oxygenate of choice because refiners could cost-effectively produce it using existing products. Since then, only a few researchers have been active in the field of higher alcohol synthesis. Some research in the 90's focused on mixed alcohols as a product of coal gasification. Other work continued in Europe, especially by Snamprogetti. Within the past 5 years, however, a desire to find alternatives for petroleum based fuels, and the increasing popularity of ethanol fuels, has again brought this research area to life.

The overall stoichiometric reaction for higher alcohol synthesis can be summarized as:

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$$

The value of "n" typically ranges from 1 to 6. The stoichiometry suggests an optimum H2/CO ratio = 2, however many of these catalysts also display significant water gas shift activity. This shifts the optimal ratio closer to 1.0 and also shifts the primary byproduct from water to carbon dioxide ($CO_2$). The overall reaction is exothermic; therefore, maintaining constant reaction temperature is an important design consideration. The reactions become more exothermic for greater values of "n". The mechanism of HAS involves a complex set of reactions with multiple pathways leading to a variety of products that are impacted by kinetic and thermodynamic constraints. Secondary reactions and other side products will depend on which catalyst system is used. Different kinetic pathways exist for each catalyst system.

## Catalysts

### *A) Modified Methanol Catalysts*

The term "modified" methanol catalyst refers to the addition of an alkali promoter and other active elements to a methanol catalyst to shift the product slate from methanol to higher branched primary alcohols. High temperature methanol catalysts typically contain Zinc (Zn) Chromium oxides (or manganese chromium oxides), while lower temperature methanol catalysts use Copper (Cu) as the active component. The reaction yields primary branched alcohols, among which 2-methyl-1-propanol (isobutanol) is a main (and thermodynamically favored) component. Aldehydes, esters, ketones, and ethers are also formed, along with large amounts of $CO_2$.

Typical high pressure and low pressure reaction conditions (as provided by Nexant) are listed in Table 2. In general there is a trade-off between maximizing CO conversion and maximizing the higher alcohol selectivity and yield.

**Table 2. "Typical" Modified Methanol Catalyst Conditions**

| | H2/CO ratio | Temp (F) | Pressure (psia) | CO conversion (per pass) | Total alcohol yield (g/kg/hr) | C2+OH Selectivity |
|---|---|---|---|---|---|---|
| High-Pres | 1 | 572-800 | 1810-3625 | 5-20% | 203 | |
| Low-Pres* | 1-1.2 | 482-752 | 725-1450 | 20-60% | | 41.9 wt% |

* Lurgi: Octamix

Snamprogetti (also referred to as SEHT – Snamprogetti, Enichem and Haldor Topsoe) and Lurgi were two of the leading technology developers of modified methanol catalysis in the 1980's and 1990's. SEHT had a MAS (Metanolo piu Alcoli Superiori - methanol plus higher alcohols) process and Lurgi developed what they called OCTAMIX, each developing pilot scale plants and data. The latest information available to NREL shows each process technology is no longer available. One technology developer still involved in this area is the Standard Alcohol Company of America. They have a bench-scale process to produce a mixed alcohols product known as Envirolene™. Envirolene is composed of methanol through octanol, with approximately 50% of the product as ethanol. The process uses a modified high pressure methanol catalyst, and the company is currently seeking funding for a pilot plant.

The proposed kinetic pathway for modified methanol catalysts to branched alcohols is through a base-catalyzed aldol condensation reaction. Carbon chain growth schemes have been developed that describe the product distribution relatively accurately.

### *B) Modified Fischer-Tropsch Catalysts*

Modified Fischer-Tropsch catalysts, on the other hand, are FT catalysts that are alkali-promoted. The two most common FT active elements are Iron (Fe) and Cobalt (Co), but Nickel (Ni) is considered to have FT activity also. The addition of the alkali promoter helps to shift the product slate from hydrocarbons to linear alcohols, although hydrocarbons remain a significant byproduct. Typical reaction conditions are 220 – 350°C (430 – 660°F) and 5-20 MPa (725 – 2900 psia). One commonly-researched catalyst system is a $MoS_2$-based system that is alkali and/or Cobalt-promoted. This has the tendency to increase ethanol and other higher alcohols selectivity. $CO_2$ is still a substantial byproduct due to water-gas shift (WGS) activity of the catalysts. Other potential byproducts include aldehydes, esters, carboxylic acids, and ketones.

The primary technology developers for these catalysts were Dow/Union Carbide (UCC) and Institut Francais du Petrole (IFP). Dow and UCC jointly developed a sulfided mixed alcohol catalyst based on molybdenum ($MoS_2$). Sulfided catalysts have the advantage of being sulfur-tolerant (up to 100 ppm) which has the potential to reduce upstream cleanup costs. IFP, in conjunction with Idemitsu Kosan (Japan), developed a process based on Cu-Co and

Cu-Ni catalyst systems. Dow built a 2-ton-per-day (TPD) demonstration plant in 1990 and IFP built a 20 barrel-per-day (BPD) pilot plant in Japan. The latest information available to NREL indicates that Dow is no longer pursuing the commercial development of their mixed alcohol process and IFP has not continued their work since building the pilot plant, and they have no commercial interest in pursuing a mixed alcohols process.

Technology developers that remain active in this area are Power Energy Fuels Inc. (PEFI), Western Research Institute (WRI), and Pearson Technologies. PEFI continues to develop the Ecalene$^{TM}$ technology and process, which is a modification of Dow's Sygmal process using polysulfite catalyst. According to Nexant, progress has not moved beyond the bench scale and a planned 500 gallon/day pilot plant is no longer being pursued. However, 2-3 other pilot plants are under funding consideration using various biomass resources. WRI had worked with PEFI in the past, however they no longer do and are conducting their own bench-scale experiments, particularly reactor and catalyst testing. Pearson technologies has developed a 30-ton-per-day biomass gasification and alcohols conversion facility in Aberdeen, MS. A project is under development by the Worldwide Energy Group and the State of Hawaii to demonstrate gasification of sugarcane bagasse and production of ethanol using the Pearson technology on the island of Kauai. Sasol (South Africa) is a world leader in FT fuels and chemicals production as well as technology development. They currently produce alcohols within their overall process. According to Sasol's website, oxygenates in the aqueous stream from their Sasol Advanced Synthol (SAS) process are separated and purified to produce alcohols, acetic acid, and ketones.

The proposed kinetics for modified FT catalysts follows different pathways than for modified methanol kinetics. Linear alcohols are formed from a classic CO insertion route for chain growth (C-C bond formation) with termination to alcohols and hydrocarbons. More complex kinetic models have reaction networks that account for the simultaneous formation of alcohols, hydrocarbons, and esters.

*C) Other Catalysts*

Some research has been conducted on alternative reaction systems for mixed alcohols synthesis. This includes more exotic catalytic elements (Ruthenium (Ru), Rhodium (Rh), Palladium (Pd)) as well as synthesis under supercritical conditions. Rh-based catalysts have been primarily developed for selective ethanol synthesis or other oxygenates. One downfall for these catalysts is their low catalytic activity which results in the need for high catalyst loadings and more drastic reaction conditions. Coupling this with their high cost and limited availability creates limited commercialization potential of these processes on a grand scale. For all Group VIII metal catalyst, CO conversion to hydrocarbons will be a significant side reaction. It has been observed that the selectivity to oxygenates of Rh-based catalysts is highly dependent on the support, promoter, and metal precursor used.

Because the focus of this work would be in the context of a thermochemical route to ethanol, a modified FT catalyst was chosen as the basis for our process design and economic analysis based on its ability to produce linear alcohols (as opposed to branched) and its potential for higher ethanol selectivities. More specifically, a moly-sulfide-based ($MoS_2$) system promoted with cobalt and alkali metal salts was chosen; a form of original Dow/UCC technology. Reaction conditions and conversion data used within the Aspen models was drawn from numerous literature sources.

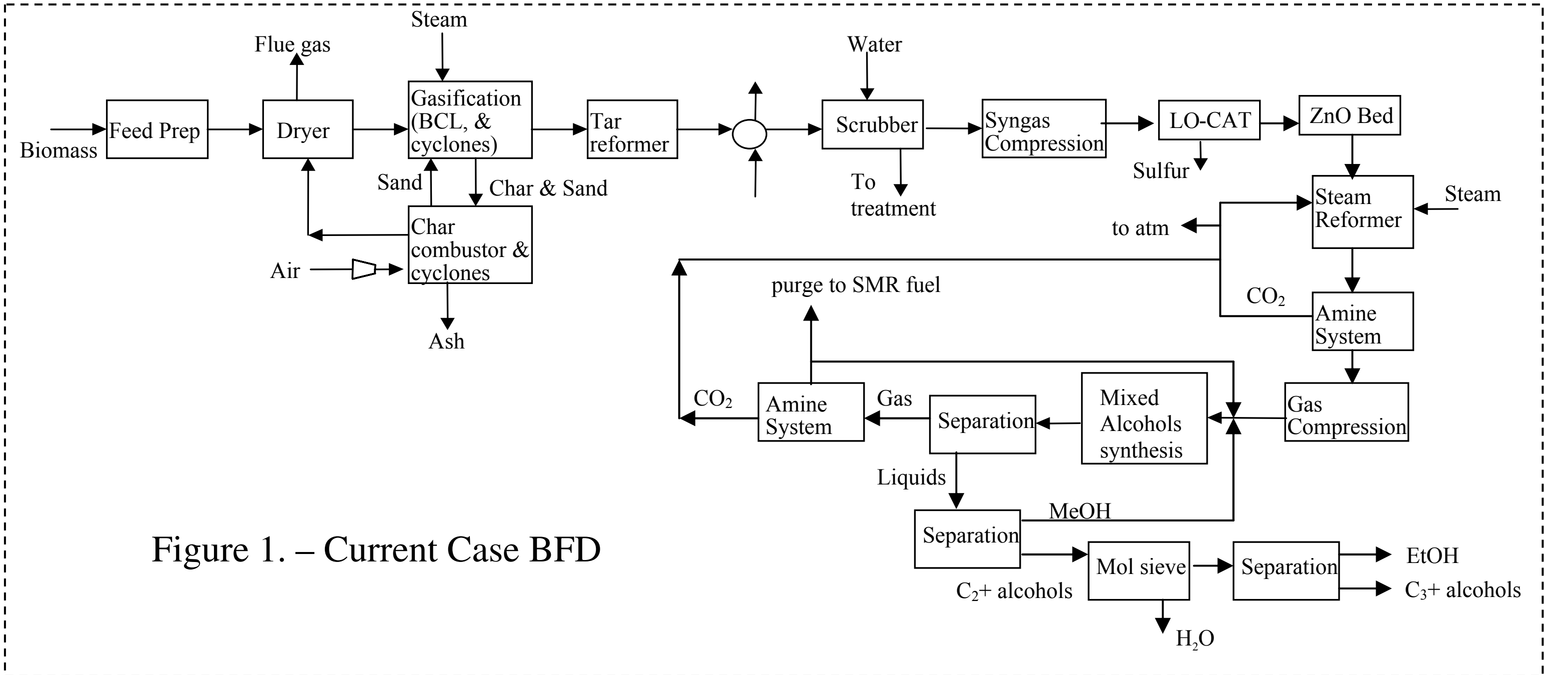

Figure 1. – Current Case BFD

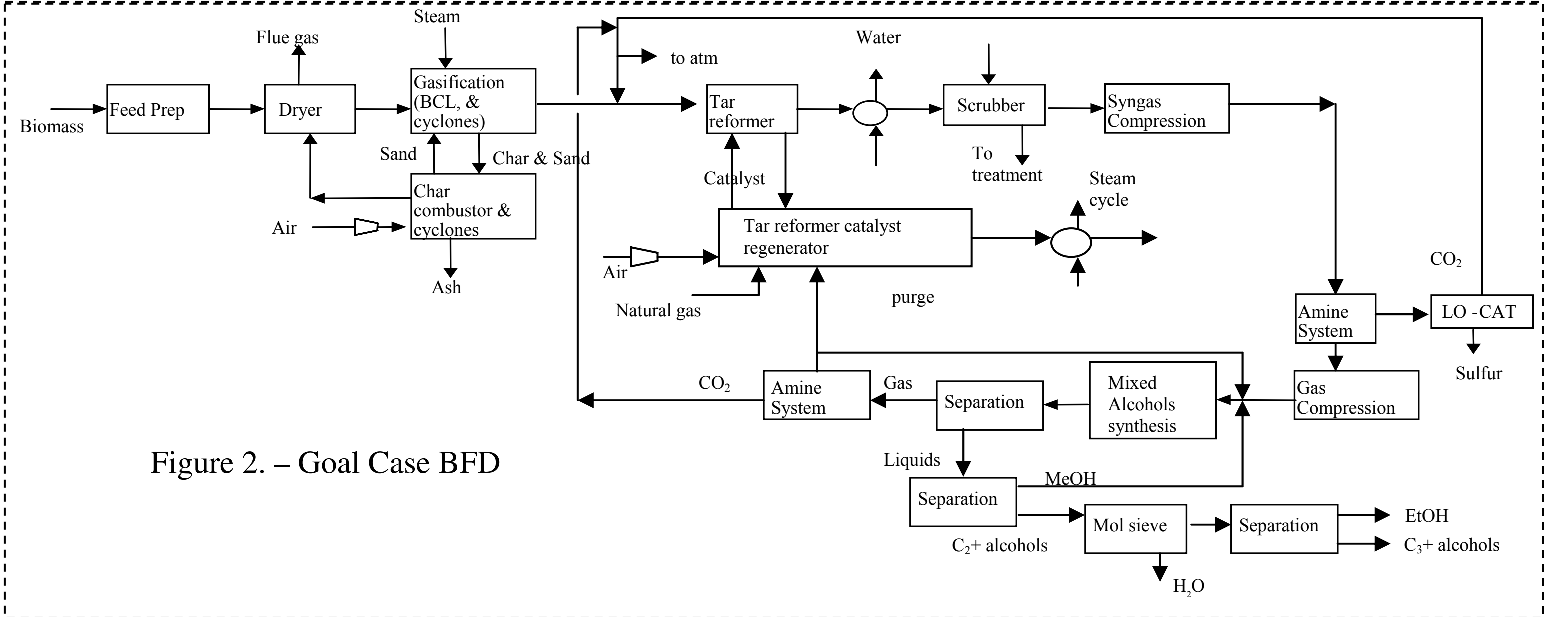

Figure 2. – Goal Case BFD

## Process Design

Figure 1 shows a block flow diagram of the overall process to convert biomass (in this case wood chips) to mixed alcohols. The as-received wood is dried down to 12 wt% moisture and then fed to a low-pressure indirectly-heated entrained flow gasifier (Battelle Columbus Laboratory, BCL). Heat for the endothermic gasification reactions is supplied by circulating hot synthetic sand (olivine) between the gasifier and char combustor. Steam is used as the gasification medium. The gas is then sent through cyclone separators to eliminate particulates.

Gas clean up and conditioning consists of a tar reformer followed by syngas quench, compression, sulfur removal, and steam methane reforming. The clean, reformed compressed syngas then goes through a chemical absorption process (amine system) to remove $CO_2$ and sulfur prior to synthesis. The gas is then compressed further to the reaction pressure and run through a fixed bed reactor. Again, a modified FT catalyst system ($MoS_2$-based) is used to optimize higher alcohol selectivity. After synthesis the gas stream is cooled to condense the liquids (mostly alcohols) product. The gas is then sent through a second amine system. The separated CO2 is recycled to the steam reformer to adjust the H2/CO ratio to design value. The rest of the gas, consisting of unconverted syngas and gaseous reaction byproducts (i.e. methane), is then recycled back to the mixed alcohol reactor in order to maximize yields. A small fraction of the recycled gas is purged as fuel to the steam methane reformer to avoid buildup of certain compounds in the recycle.

*Table 3 – Mixed Alcohol Synthesis Reaction Conditions and Specified conversions*

| Catalyst | Mod. FT ($MoS_2$ / Co / K) | CO2-free Alcohol Selectivity = 80% | |
|---|---|---|---|
| Temperature (°C) | 300 | | |
| Pressure (PSIA) | 2000 | | |
| Gas Hourly Space Velocity ($hr^{-1}$) | 3000 | | |
| Reactor Design | Fixed Bed | | |
| $H_2$/CO Ratio | 1.2 | | |
| $CO_2$ concentration entering | 2 wt% | | |
| mol% CO conversion (per pass) to: | | Selectivity (CO2-free) | Selectivity (overall) |
| $CO_2$ | 13.0% | -- | 34.2% |
| $CH_4$ | 4.5% | 18% | 11.9% |
| $C_2H_6$ (ethane) | 0.5% | 2% | 1.3% |
| Methanol | 4.1% | 16.4% | 10.8% |
| Ethanol | 11.4% | 45.6% | 30.0% |
| Propanol | 3.0% | 12% | 7.9% |
| Butanol | 1.0% | 4% | 2.6% |
| Pentanol & higher | 0.5% | 2% | 1.3% |
| **Total** | **38%** | **100%** | **100%** |

Table 3 shows the mixed alcohol synthesis conditions used in the model, as well as the specified conversions. The high reaction pressure (2000 psia) necessitates significant compression within the process. The $CO_2$ concentration entering the reactor is kept low (2 wt%) because concentrations above 5% have been shown to impede conversion and/or selectivity. As discussed previously, the $H_2/CO$ ratio is slightly above 1.0 due to the WGS activity of the catalyst. A-38% per pass total CO conversion is specified. Excluding $CO_2$, CO is converted to either alcohols or hydrocarbons (methane, ethane). On a $CO_2$-free basis, the total selectivity to all alcohols is 80% and selectivity to hydrocarbons is 20%. The highest specific selectivities are for ethanol and methanol.

Methanol is distilled from the condensed liquid product and recycled to the mixed alcohol reactor as well to shift conversion towards the higher alcohols. In this fashion, methanol can be recycled to near extinction. The remaining alcohols product, mostly ethanol, propanol, n-butanol, and pentanol, is dewatered using molecular sieve technology to meet fuel specifications.

Because of the lack of commercial development for mixed alcohols technology, very little process design information was available. Therefore NREL spent a significant amount of time and in-house engineering expertise to examine a multitude of design options, especially with regards to the amount of recycle, the destination of recycled material, and the cost implications of doing each. As stated earlier, a second case (goal case) was developed to demonstrate the impact of tar reformer improvements on the overall process design. Because more methane is converted within the tar reform, a steam methane reformer no longer becomes necessary. The block flow diagram is shown in Figure 2. In this design, the amine-separated CO2 (minus sulfur) is recycled to the tar reformer. In both designs, a steam cycle is integrated with the process to provide process steam and power demands. If more power is required than generated, it is purchased from the power grid.

Detail economics and sensitivity analyses are included in the slide presentation.

## References

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