

Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment

Task 9: Mixed Alcohols From Syngas — State of Technology

Nexant Inc.
San Francisco, California

Subcontract Report
NREL/SR-510-39947
May 2006

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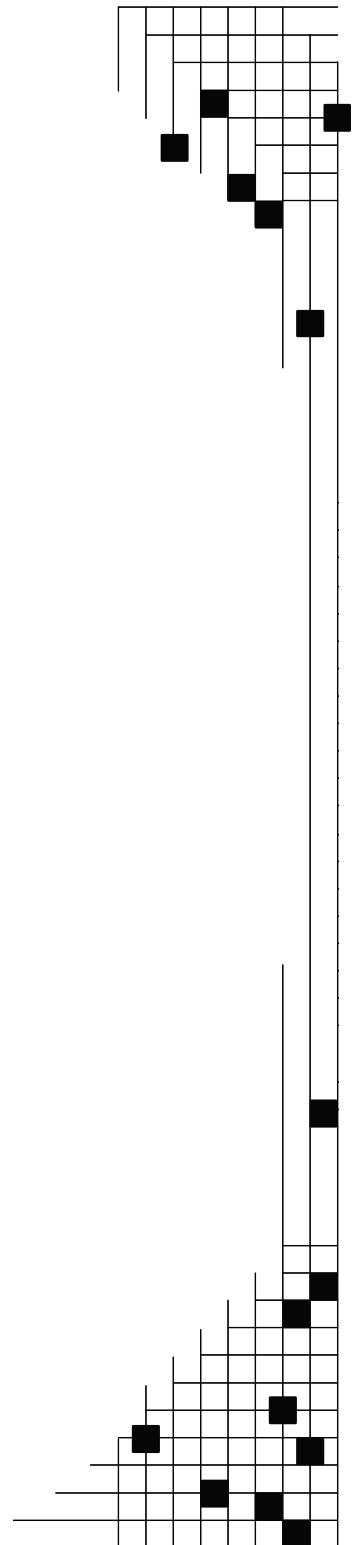
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Executive Summary

Due to limited incentives and significant risks involved in the mixed alcohols process, little commercial development has occurred this decade. Most original technology developers, who first investigated the technology in the mid-1980s, have since abandoned the technology. However, new catalysts, new project developers, and a desire to find alternatives for petroleum based fuels and oxygenates has brought new life to this technology.

The major catalysts commercially available for mixed alcohol production from syngas are modified methanol catalysts, modified Fischer-Tropsch catalysts, and alkali-doped molybdenum catalysts. Recent work has also been performed on zirconium catalysts that show potential for process improvements. None of the catalysts investigated are clearly superior to the others; criteria prioritization must be performed by project developers to determine which catalyst aspects are of greatest importance. While no catalyst had a significant advantage in syngas conversion, molybdenum catalysts performed well on alcohol yield, selectivity, and impurity resistance criteria. A more direct comparison of each catalyst on a weighted set of process criteria would be helpful to better defining R&D plans.

Recent research efforts have focused on changing base catalyst formulations instead of developing entirely new catalysts. These efforts have included doping of catalysts with different metals, novel catalyst preparation techniques, optimizing process conditions, and new catalyst support materials. While many of these research efforts have improved catalyst performance, an evaluation of the economics of each improvement needs to be performed.

The tolerance of modified methanol and Fischer-Tropsch catalysts to sulfur remains very low (<1 ppm). Sulfided catalysts represent an improvement in this area, but it is unclear if this improves the economics of the process. If required to maintain between 50 and 100 ppm of sulfur in the syngas, only very small improvements in the overall process economics are possible. In addition, low sulfur requirements, especially to H₂S and mercaptans, for transportation and chemicals applications of the mixed alcohol product may require additional cleanup anyway, potentially eliminating any economic advantage.

The technical and economic risks include feasibility to produce the desired product slate, scale-up considerations, designing for severe process conditions, catalyst sensitivities, competitiveness versus petroleum fuels, and catalyst prices. Studies have shown that current mixed alcohol technologies can compete with wholesale gasoline prices at \$1.25 to \$1.70 per gallon, assuming \$0/ton feedstock prices and no production credits. Consideration must be made for the impacts this product will have on transportation fuel specifications, especially octane, volatility, sulfur, and corrosion. Fluctuations in price for rare and high

demand metals also add considerable risk to the commercial feasibility of this process.

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Introduction and Methodology

This deliverable is for Task 9, Mixed Alcohols from Syngas: State of Technology, as part of NREL Award ACO-5-44027, “Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup and Oxygen Separation Equipment”. Task 9 supplements the work previously done by NREL in the mixed alcohols section of the 2003 technical report entitled, “Preliminary Screening – Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas”. It is assumed that NREL’s knowledge of higher alcohol synthesis is extensive, as demonstrated in the 2003 technical report. Thus, information presented by NREL in 2003 that is still current will not be elaborated upon in detail. Rather, confirmation will be provided, along with information on recent developments of higher alcohol synthesis technologies.

This report updates the preliminary NREL work in the following three areas: the current state-of-the-art technologies for the production of mixed alcohols from syngas; interaction between different mixed alcohol catalysts and sulfur removal technologies; and areas of technical and economic risk in the mixed alcohols process. Suggestions are made for the appropriate sulfur removal technologies for different catalysts, with recommendations for suitable combinations for NREL designs. Finally, the risks section gives a comprehensive overview of R&D requirements, policy drivers, and economic hurdles that must be overcome to bring about commercialization of the mixed alcohol from biomass technologies.

Besides using Nexant’s previous experience and information database, the current information was obtained by conducting literature searches, contacting commercial vendors of the mixed alcohol technologies, and using the Nexant developed IGCC economic model.

1.1 Technology Description

In the early 1980's commercial chemical companies, such as Dow and Snamprogetti, patented their own higher alcohol synthesis (HAS) technologies in response to the oil embargo of the 1970's and the phase out of lead as an octane enhancer in gasoline. However, commercial interest decreased with the increased supply of cheap petroleum and the use of methyl tert-butyl ether (MTBE) as an octane booster. Because MTBE has excellent blending properties and good economics, it has become the primary oxygenate chosen by refineries outside of the Midwest to meet the reformulated gasoline standards of the Federal Clean Air Act Amendments of 1990. The recent phase-outs of MTBE from much of the gasoline pool has renewed interest in ethanol and mixed alcohols as an alternative oxygenate.

As of April 2005, there are no commercial plants that exist solely to produce mixed alcohols in the C₂ to C₆ range from syngas. In fact, many of the companies that had once pursued research to commercialize the production of mixed alcohols have now abandoned it. The status of these commercialization attempts will be further discussed in Section 1.4.

The main process steps for higher alcohol synthesis do not differ from what was outlined by NREL in 2003. The main steps are synthesis gas production, followed by gas clean up and conditioning, alcohol synthesis, and product purification.¹ This is a typical route regardless of how the syngas is used. The items that are unique to mixed alcohol production are the process conditions for product synthesis, level of clean up (depending on the catalyst chosen), and purification/recycle steps.

It is worth mentioning that Sasol has commercial plants in South Africa that utilize the mixed alcohol by-product of their coal to Fischer-Tropsch liquids process for other commercial needs. However, this is not optimized for mixed alcohols production², and, thus, does not qualify as a commercial plant for mixed alcohol production.

¹ U.S. Department of Energy. National Renewable Energy Laboratory. "NREL/TP-510-34929: Preliminary Screening – Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas." Golden, CO.: December 2003.

² Sasol currently has an FT facility that yields 4800 BPD of alcohols comprised of 2% methanol, 66% ethanol, and the remainder higher alcohols. However, the stream is used predominantly as a petrochemical intermediate. Information from Dr. Michael S. Graboski, "An Analysis of Alternatives for Unleaded Petrol Additives for South Africa", UNEP sponsored report, May 2003.

1.2 Catalysts

Higher alcohol synthesis catalysts have undergone a number of improvements in the past few years. The majority of the incremental improvements relate to better characterization of higher alcohol yields for different catalyst compositions. In addition, potentially significant improvements in yields have come from research done on new catalyst formation processes.

This additional work that has been performed on mixed alcohol catalysts requires new categorization. Three of the four categories remain the same as in the NREL 2003 technical report; one category was expanded to include all molybdenum-based catalysts, and another category was added for additional catalysts. The categories are as follows:

1. Modified high pressure methanol synthesis catalysts – alkali-doped ZnO/Cr₂O₃
2. Modified low pressure methanol synthesis catalysts – alkali-doped Cu/ZnO and Cu/ZnO/Al₂O₃
3. Modified Fischer-Tropsch catalysts – alkali-doped CuO/CoO/Al₂O₃
4. Alkali-doped molybdenum based catalysts
5. Other catalysts, mainly ZrO₂ based

If some of the new research continues to yield improvements and advances over existing catalysts, it may be possible for molybdenum-based catalysts to be more active than oxide-based catalysts if prepared under new methods. This is an area that NREL should follow closely to assure the most up-to-date data is included in mixed alcohol designs.

1.2.1 Modified High Pressure Methanol Synthesis Catalysts

Modified high pressure methanol synthesis catalysts are primarily alkali doped ZnO/Cr₂O₃. The typical process conditions are summarized in Table 1. Unless otherwise noted, data for process conditions tables are derived from the 2003 NREL mixed alcohols analysis:

H ₂ /CO Ratio	T (F)	P (psia)	CO ₂ Sensitivity	CO conversion (per pass)	Main Product Yield	Total alcohol STY (g/kg _{cat} /hr)
1	572 - 800	1810 - 3625	significant at 6%	5 - 20%	Branched Primary Alcohols	203 ³

³ W.S. Epling, et. al, "Higher alcohol synthesis reaction study VI: effect of Cr replacement by Mn on the performance of Cs- and Cs, Pd-promoted Zn/Cr spinel catalysts", Applied Cat. A: General, (1999) 335-343.

The benefits of these catalysts include:

- Significant data exists to be able to predict the performance and effectiveness of Zn/Cr catalysts.
- Highest isobutanol production rates of any catalyst group.

The drawbacks to these catalysts include:

- Significantly decreased C₂+OH yields with CO₂ rich (~6%) syngas stream.⁴
- High pressure requirements.

The group of George W. Roberts of North Carolina State University has published research dealing with isobutanol synthesis from such ZnCr catalysts.⁵ His work has been directed towards the use of ZnCr catalysts for HAS in slurry reactors and is further discussed in section 1.3.2. His work was not discussed in the 2003 technical report, but NREL may be interested in his attempts to use ZnCr in a slurry reactor to increase selectivity and yields of higher alcohols. However, no such improvements of selectivity or yields have been made at this time.

1.2.2 Modified Low Pressure Methanol Synthesis Catalysts

The difference between modified low pressure and high pressure methanol synthesis catalysts is whether the catalyst formulation contains copper. The typical process conditions are summarized in Table 2. The ranges given cover the conditions that most catalysts of this type would operate under.

Catalyst	H ₂ /CO Ratio	T (F)	P (psia)	CO Conversion (per pass)	C ₂ +OH Selectivity	Primary Product Yields
Lurgi: Octamix	1-1.2	482-752	725-1,450	20-60%	41.9 wt%	

The benefits of these catalysts include:

⁴ E. Tronconi, L. Lietti, P. Forzatti, and I. Pasquon, "Synthesis of Alcohols from Carbon Oxides and Hydrogen .17. – Higher Alcohol Synthesis over Alkali Metal-Promoted High- Temperature Methanol Catalysts." *Applied Catalysis* 47, no.2, (1989): 317-333.

⁵ Xiaolei Sun, N.W. Jones, J.C. Gesick, L. Xu, and G.W. Roberts, "Liquid/Catalyst Interactions in Slurry Reactors: Changes in Tetrahydroquinoline Composition during Methanol Synthesis over Zinc Chromite", *Applied Catalysis A. General* 231 (2002): no. 269.

- Lower pressure requirements than high pressure methanol catalysts.
- Effectiveness of process has been detailed in the literature.⁶

The drawbacks to these catalysts include:

- High CO conversion can decrease higher alcohol selectivity and yield.
- Lower production of higher alcohols and other oxygenated products than modified high pressure methanol synthesis catalysts.⁷
- Cu sintering limits the upper temperature of the process.

NREL's 2003 technical report mentions that modified low pressure methanol catalysts mainly produced primary alcohols. In addition, literature indicates that modified low-pressure methanol synthesis catalysts also produce branched primary alcohols as a significant product. Specifically, K-promoted/Cu/ZnO/Al₂O₃ catalysts fall into a group of catalysts that predominantly produce branched alcohols, such as isobutanol.⁸ This is particularly important for understanding the mixed alcohol product composition that will be produced by this catalyst.

Also, recent research conducted by Ismail Boz of Istanbul University has improved the understanding of modified low pressure methanol catalysts with Co and K added. The research found that a 5% K₂O promoter concentration yields the greatest higher alcohol selectivity for a Co₂O₃/CuO/ZnO/Al₂O₃ catalyst, and that 563 K maximizes higher alcohol selectivity over methanol with an H₂/CO = 2 at 580 psia.⁹ In addition, using lower space velocities than those used for methanol synthesis can improve higher alcohol selectivity. Furthermore, increasing CO conversion beyond 10%, which is shown to be dependent on temperature, reduces higher alcohol selectivity and yield in favor of hydrocarbons. Thus, in order to increase higher alcohol selectivity and yield with a modified low pressure methanol synthesis catalysts, it will be necessary to lower the space velocity and to use the correct amount of promoter. Also, it is important to recognize that there may be a trade off between maximizing CO conversion and maximizing the higher alcohol selectivity and yield.

⁶ Refers to articles referenced in National Renewable Energy Laboratory paper. These include: Elliott, D.J. and Pennella, F. (1988); Nunan et al. (1989); Smith and Anderson. (1984). Smith and Klier (1992).

⁷ P. Forzatti, E. Tronconi, and I. Pasquon. "Higher Alcohol Synthesis" *Catalysis Reviews-Science and Engineering* 33, no.1-2 (1991): 109-168.

⁸ J.M. Campos-Martin, A. Guerrero-Ruiz and L.G. Fierro, *J. Catal.* 156 (1995) 208.

⁹ Ismail Boz. "Higher Alcohol Synthesis over a K-promoted Co₂O₃/CuO/ZnO/Al₂O₃ catalyst." *Catalysis Letters*. Vol. 87, Nos. 3-4, April 2003.

1.2.3 Modified Fischer-Tropsch Catalysts

The majority of previous information available on the modified Fischer-Tropsch catalyst originated from the commercial process developed by the Institut Francais de Petrole (IFP) over 15 years ago. There have, however, been recent independent developments related to new catalyst preparation techniques.

The general process conditions are summarized in Table 3. Depending on the type of alcohols desired, H₂/CO ratio, temperature, and pressure can all be manipulated to promote heavier or lighter alcohol production.

Catalyst	H₂/CO Ratio	T (F)	P (psia)	CO Conversion (per pass)	C₂+OH Selectivity	Primary Product Yields
IFP	1-2	500-608	850-1450	5-30%	30-50%	Straight-chained alcohols

The benefits of these catalysts include:

- Greater selection for higher linear alcohols than modified methanol processes.
- New catalyst preparation techniques can significantly improve CO conversion rates.

The drawbacks of these catalysts include:

- Decreasing H₂/CO ratio increases higher alkane yield.¹⁰ This should not be an issue with biomass because biomass tends to have a high H₂/CO ratio relative to coal derived syngas.

Different catalyst preparation techniques have shown different conversion rates for the syngas feed. The typical method of catalyst preparation has been co-precipitation. However, alternative techniques for catalyst preparation have been shown to increase overall conversion rates. For example, researchers have recently claimed that preparing catalyst with the sol-gel/oil-drop method can increase CO conversion rates by ~14 - 30% over catalysts prepared by co-precipitation methods. This has important implications when considering the maximum yield of mixed alcohols a process can expect from a given modified Fischer-Tropsch catalyst.

¹⁰ S. Naidu, U. Siriwardane, "Novel Preparation and Magneto Chemical Characterization of Nano-Particle Mixed Alcohol Catalysts" DOE Grant Number: DE-FG26-00NT40836. 8/31/2003.

Work carried out by Arislete Dantas de Aquino from Brazil in 2001 has helped characterize the effect of alkali metals on the higher alcohol yield and selectivity of Al-Cu-Co based catalysts.¹¹ Specifically, Li, Na, K, and Cs were tested and the following information was found:

- Li increased selectivity of methanol and C₂-OH yield while decreasing that of hydrocarbons
- Na increased catalyst deactivation, but the selectivity of hydrocarbon and alcohol remained relatively constant.
- K reduces overall higher alcohol yield and produces only methanol and ethanol. It also reduces hydrocarbon yield.
- Cs considerably lowers alcohol yield selectivity.

These results should be taken into consideration if a modified Fischer-Tropsch catalyst is used. From the current research, it appears that the use of Li as a promoter would have the most beneficial effect upon alcohol yield and selectivity of the available alkali promoters.

1.2.4 Alkali-Doped Molybdenum-Based Catalysts

The category of alkali-doped sulfide catalysts has been expanded to include all molybdenum-based catalysts. The discussion will be divided between sulfided molybdenum-based catalysts and pre-reduced catalysts, expanding the coverage of this catalyst type from NREL's 2003 analysis. Table 4 summarizes the basic process conditions for sulfided catalysts.

Catalyst	H ₂ /CO Ratio	T (F)	P (psia)	CO Conversion (per pass)	Alcohol Selectivity	Alcohol Yield (g/kg/hr)
General Literature	1	500-662	435-2538	10%	75-90%	
Dow				<40% ¹²		
K-Co-MoS ₂ ¹³	2	581	1515	39%	75.7%	115
K-Co-Mo/Al ₂ O ₃ ¹⁴	2	650	1515	-	59%	370
K-Co-Mo/SiO ₂ ¹⁵	2	482	725	7.2%	59%	370

¹¹ Arislete Dantas de Aquino, and Antonio Cobo, "Synthesis of higher alcohols with cobalt and copper based model catalysts: effect of the alkaline metals." *Catalysis Today*, 65, no. 2-4, 2001, 209-216.

¹² G. Quarderer, "Mixed Alcohols from Synthesis Gas". April 1986. 78th Spring National AIChE Meeting.

¹³ R.R. Stevens, U.S. Patent 4,882,360, 1989.

¹⁴ D.A. Storm, Top. *Catal.* 2 (1995): 91.

¹⁵ K. Fujimoto, T. Oba, *App., Catal.* 13 (1985): 289.

The benefits of these catalysts include the following:

- The sulfide-based catalysts require 50-100 ppm H₂S in syngas stream to maintain the sulfidity of the catalyst. Thus, they are sulfur resistant, and sulfur clean up costs may be able to be reduced.¹⁶
- The catalysts are less sensitive to CO₂ in the syngas stream than other catalysts. However, catalysts activity can still be inhibited with high amounts of CO₂ (>30%).¹⁷
- Carbon laydown (coking) does not become a problem even with low H₂/CO ratio (i.e. <2).¹⁸
- Primarily produce non-branched linear alcohols.

These catalysts have the following drawbacks:

- Oxide-based catalysts tend to be more active than these sulfide-based catalysts.¹⁹

1.2.4.1 Molybdenum-Sulfide Catalysts

Catalyst Characterization

There has been important research recently conducted on alkali-doped sulfide catalyst for higher alcohol synthesis. The sulfide-based catalysts have been better characterized, and the new developments may enable increased higher alcohol yields. As an example, when K and Cs are used as promoters on a Co-MoS₂/clay catalyst, the alcohol yield was found to increase with reaction temperature; however, alcohol selectivity decreased with an increase in reaction temperature.²⁰

Further developments have characterized the effect of alkali promoters on the yield and composition of C₂+OH. The space-time yield of C₂+OH was strongly

¹⁶ P. Courty, P. Chaumetter, C. Raimbault, and P. Travers, "Production of methanol-higher alcohol mixtures from natural gas via syngas chemistry." *Revue de l'Institut Francais du Petrole*, 45, no.4 (1990): 561-578.

¹⁷ R.G. Herman "Chapter 7 – Classical and Non-classical Routes for Alcohol Synthesis." *New Trend in CO Activation*, 265-349, (New York: Elsevier, 1991).

¹⁸ G. Quarderer, *ibid*.

¹⁹ R.G. Herman, "Advances in catalytic synthesis and utilization of higher alcohols." *Catalysis Today* 55 no. 3, 200: 233-245.

²⁰ J. Iranmahboob, H. Toghiani, D. Hill. "Dispersion of alkali on the surface of Co-MoS₂/clay catalyst: a comparison of K and Cs as a promoter for synthesis of alcohol." *Applied Catalysis A: General*. 247, no.2 (2003): 207-218.

correlated with the alkali metal promoter to MoS₂ ratio (M/MoS₂).²¹ The maximum space-time yield was found to be at a maximum around an M/MoS₂ ratio of ~.2 independent of the alkali metal promoter chosen. Of the alkali metal promoters chosen (M: K, Rb, and Cs), the Rb/MoS₂ catalyst with an Rb/Mo ratio of .25 demonstrated the highest space-time yield of C₂+ alcohol, and it also had the highest chain growth probability, .35. Finally, it was found that MoS₂ catalysts could achieve higher alcohol yields than Cu based catalyst, but it requires pressures greater than 1,450 psia to achieve.

Catalyst Formation

Novel developments in catalyst formation techniques have contributed to potentially significant improvements in higher alcohol synthesis yields. The traditional way to prepare MoS₂ catalyst is thermal decomposition or reduction of (NH₄)₂MoS₄ (ATTM), where ATTM refers to ammonium tetrathiomolybdate. However, recent techniques have been identified that could increase the surface area of the catalyst significantly by preparing the catalyst by the reduction of ATTM in the presence of water.²² The technique used involves the presence of a long chain alkane, tridecane, to increase the surface area of MoS₂ by nearly a factor of four, increasing catalyst activity.

1.2.4.2 Pre-Reduced Molybdenum-Based Catalysts.

Catalyst Characterization

A large amount of work has also been done on pre-reduced molybdenum-based catalysts. For example, a Mo-Ni-K/SiO₂ catalyst was found to perform the best of other pre-reduced molybdenum-based catalysts as measured by largest space-time yield.²³ Additional work on a similar Mo-Ni-K/SiO₂ catalyst demonstrated that space time yield of alcohols could be further increased with a novel method of catalyst formation known as Metal Oxide Vapor Synthesis (MOVS).²⁴ Given the promise of Mo-based catalysts, the Division of Fossil Energy under the National Energy Technology Laboratory has recently sponsored work on higher alcohol synthesis from Mo-based catalyst.

²¹ Naoto Koizumi, et. al., "Development of sulfur tolerant catalysts for the synthesis of high quality transportation fuels." *Catalysis Today* 89 (2004): 465-478.

²² Y. Yoneyama, C. Song, *Catalysis Today* 50 (1999): 19-27

²³ T. Tatsumi, A. Muramatsu, "Molybdenum Catalysts for synthesis of mixed alcohols from synthesis gas." *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)* 35, 1992: 233

²⁴ E.C. Alyea, D. He, J. Wang "Alcohol Synthesis from syngas. I. Performance of alkali-promoted Ni-Mo (MOVS) catalysts." *Appl. Catal. A: General* 104, (1993): 77.

Recent DOE sponsored research on calcined Mo-Ni-K/C catalysts have helped characterize the higher alcohol synthesis that can be achieved by this catalyst. Four major areas of interest were elaborated upon by this research.

1. The space-time yield of both alcohols and hydrocarbons are increased with an increase in reaction temperature; however, this causes an overall decrease in total alcohol selectivity as temperature increases.²⁵
2. Addition of Ni and K increases the total alcohol selectivity, but the catalysts must, in general, be reduced first.
3. Alcohol yield decreases with increasing partial pressure of H₂ and increases with greater partial pressures of CO.
4. Increased gas hourly space velocity (GHSV) is favorable for total alcohol yields. The general trends of the Mo-Ni-K catalyst supported by carbon are very similar to that seen in molybdenum-sulfide catalysts already discussed.

The information obtained by this research helps establish the process conditions—H₂/CO ratio, GHSV, Temperature—and catalyst composition that will optimize higher alcohol yields and selectivity for the desired product slate.

Catalyst Formation and Support

Research has also been conducted on the catalyst support structure and preparation for molybdenum catalysts. For instance, higher catalytic activity resulted from a Mo-K catalyst supported by activated carbon compared to a Mo-K catalyst supported by Al₂O₃.²⁶ This research done has also revealed that the space-time yield of alcohol synthesis is optimized at MoO₃ loading of 48%. Similar to the research conducted on sol-gel preparation techniques for modified Fischer-Tropsch catalysts, the effect of sol-gel preparation of a K-Co-Mo/C catalyst was also studied. The sol-gel method was shown to produce a high alcohol yield, particularly for C₂+OH.²⁷

An additional area of potential interest is the effect of metal doping. In one study, the addition of rhodium as a promoter to a Mo-K/ γ -Al₂O₃ catalyst nearly tripled the space-time yield of higher alcohols from 370 to 1,100 g/(hr*kg) of

²⁵ Lawrence Norcio, et al. "Synthesis of Hydrocarbons and Alcohols from Syngas." C1 Chemistry for the Production of Clean Liquid Transportation Fuels and Hydrogen: DOE 2002 Annual Report. DE-FC26-99FT40540.

²⁶ Zhong-rui Li, Y Fu, M. Jiang, T. Hu, T. Liu, and Y. Xie, "Active Carbon Supported Mo-K Catalysts Used for Alcohol Synthesis." *Journal of Catalysis*, 199, 2, (2001): 155-161.

²⁷ J. Bao, Y Fu, Z. Sun, C. Gao, "A highly active K-Co-Mo/C catalyst for mixed alcohol synthesis from CO + H₂." *Chem. Commun.* no. 6 (2003): 746-747.

catalyst.²⁸ Additional work has been done characterizing the increased alcohol selectivity that K doping has upon a Mo/AC catalyst.²⁹ These results could possibly increase the attractiveness of sulfide-based catalysts that are promoted by rhodium and potassium; however, rhodium has previously been optimized for ethanol synthesis only, and it is much more expensive than potassium, as will be discussed in Section 3.3.

1.2.5 Other Catalysts

There are a variety of other catalysts that have some capability to produce higher alcohols, but they are not given much attention because their overall selectivity for higher alcohols has historically been low or they have been developed for other end products. For example, rhodium based catalysts were briefly mentioned in the 2003 technical report as such a catalyst group, yet they are more capable of yielding ethanol than being effective for higher alcohol synthesis.

Other Sulfide Based Catalysts

The higher alcohol yields of catalysts similar to molybdenum sulfide-based catalysts have also been explored. Because research had only been previously conducted with Mo and W sulfide catalysts, the space-time yields of Rh, Pd, Re and Os sulfide catalysts were tested in recent research. Rhodium was found to have a higher alcohol formation rate than Mo and W.³⁰ This research suggests that rhodium sulfide catalysts could be superior, in terms of alcohol yields, for higher alcohol synthesis. However the high costs of rhodium would likely prevent its usefulness as a widespread catalyst.

ZrO₂ Catalysts

Another new catalyst type are ZrO₂-based catalysts. A ZrO₂ based catalyst, promoted by Pd, has proven itself as an effective catalyst for the production of ethanol or isobutanol.³¹ The study also demonstrated that adding methanol or 1-

²⁸ D.A. Storm, "The production of higher alcohols from syngas using potassium promoted Co/Mo/Al₂O₃ and Rh/Co/Mo/Al₂O₃." *Topics in Catalysis*. 2 (1995): 91.

²⁹ X. Li, L. Feng, L. Zhang, D. Dadyburjor, E. Kugler, "Alcohol Synthesis over Pre-Reduced Activated Carbon-Supported Molybdenum-Based Catalysts." *Molecules* 8 (2003): 13-30.

³⁰ Naoto Koizumi, et. al. "Development of sulfur tolerant catalysts for the synthesis of high quality transportation fuels." *Catalysis Today* 89 (2004): 465-478.

³¹ Daiping He, Y. Ding, H. Luo, and Can Li, "Effects of Zirconia phase on the synthesis of higher alcohols over zirconia and modified zirconia." *Journal of Molecular Catalysis A: Chemical*. 208, Issues 1-2. (2004): 267-271.

propanol into the feed of the reactor can increase isobutanol yields by 17% and 72%, respectively. Representative process conditions are contained in Table 5³²:

Catalyst	H ₂ /CO Ratio	Temp. (F)	Pressure (psia)	CO Conversion	Alcohol Selectivity	Alcohol Yield (g/ml/hr)	Primary Products
K-PdCuMn ZrO ₂	.9	608-671	1740	22.6-29.3 mol %	37.7-51.7	.41-.81	71.3 – 88.4 wt% CH ₃ OH
Li-PdZrO ₂	2	752	1160	7-8 %		146.3 g/kg/hr	

The C₂+OH selectivity of ZrO₂ catalysts modified with a number of metals, copper, iron, cobalt, nickel, and manganese, has also been studied. The addition of manganese to the catalyst was found to increase the higher alcohol selectivity and suppress the formation of methane. Iron addition, in general, hindered mixed alcohol formation, and increased the selectivity to hydrocarbons.³³ This should not be surprising, as iron is a common catalyst for the production of Fischer-Tropsch liquids. Adding Ni and Co made improvements in the higher alcohol selectivity of a Cu/Mn/ZrO₂ catalyst to the catalyst.³⁴ The use or absence of these metals in a Cu/Mn/ZrO₂ catalyst could significantly increase higher alcohol selectivity. Ni and Co should be present in the catalyst in the right proportion while minimizing the presence of Fe.

1.3 Reactors

Standard fixed-bed reactors are currently employed in experimental HAS systems. Investigations have been made into two novel processes, multiple reactors and slurry reactors, to improve system performance. While neither of these are commercially available, the discussion below provides an update for the status of both technologies.

1.3.1 Multiple Reactors

Because HAS is an extremely exothermic process, there is interest to optimize the heat removal process. A multiple reactor design, or a “double bed” configuration, has been one idea explored to accomplish this. In this

³² C. Yang, Minggui Lin, Z. Ma, W. Li, Y. Sun, M. He, “Novel Catalyst and Process Development for CO Hydrogenation”. State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences.

³³ Run Xu, C. Yang, W. Wei, W. Li, Y. Sun, and T. Hu, “Fe-modified CuMnZrO₂ catalysts for higher alcohol synthesis from syngas.” *Journal of Molecular Catalysis A: Chemical* 221. (1-2). (2004): 51-58.

³⁴ N. Zhao, R. Xu, and W. Wei, “Cu/Mn/ZrO₂ catalyst for alcohol synthesis by Fischer-Tropsch modified elements.” *Reaction Kinetics and Catalysis Letters*. 75 (2), (2002). 297-304.

configuration, methanol production from syngas can be optimized in the first bed with a Cu catalyst and low temperatures, and the higher alcohol synthesis yield can be maximized in a second reactor with a higher temperature and a non-Cu Zn-chromite based catalyst.³⁵

Promising work on optimizing a double-bed reactor design has been conducted at Lehigh University. The first reactor was optimized for the production of short-chain alcohols over a Cs-promoted Cu/ZnO/Cr₂O₃ catalyst, and the second reactor was optimized to synthesize isobutanol over a Cs-promoted ZnO/Cr₂O₃ catalyst. The synergy of these two tubular bed reactors increased isobutanol production by 62% above what could be obtained with two reactor beds with the Cu catalyst alone³⁶. Further research was halted in 1996 because the process was not considered economically promising at the time.

1.3.2 Slurry Reactors

The use of slurry reactors is of considerable interest for higher alcohol synthesis, because the formation of higher alcohols is extremely exothermic requiring significant heat removal. Breman conducted earlier research of higher alcohol synthesis in slurry reactors compared to fixed bed reactors. His work demonstrated that the presence of n-octacosane (a type of paraffin crystal) as a slurry liquid lowered higher alcohol to methanol selectivity and increased hydrocarbon yields.³⁷ Over the past decade, the Roberts group at North Carolina State University has conducted a significant amount of research on alcohol synthesis in high temperature, 650 K, slurry bed reactors with a ZnCr catalyst. They have utilized three different slurry liquids for testing: tetrahydroquinoline (THQ), tetrahydronaphthalene (Tetralin), and decahydroquinoline (Decalin).³⁸ This could be of future interest if significant breakthroughs can be made, but too little data is currently available to make this a practical choice for higher alcohol designs.

1.4 Technology Developers

The development of a commercialized higher alcohol synthesis process has not significantly changed since the 2003 NREL report. No commercial plants have been built, and no pilot plants have been funded. In fact, some of the most

³⁵ K.A.N. Verkerk, B. Jaeger, C.H. Finkeldi, and W. Keim, W. "Recent developments in isobutanol synthesis from synthesis gas." *Applied Catalysis, A: General* 186 (1,2)(1999): 407-431.

³⁶ United States Department of Energy. "Development of Alternative Fuels and Chemicals from Synthesis Gas" DE-FC22-95PC93052. May 2003.

³⁷ B.B. Breman, A.A.C.M Beenackers, H.A. Schuurmann, H.A., E. Oesterholt, "Kinetics of the gas-slurry methanol-higher alcohol synthesis from CO/CO₂/H₂ over a Cs-Cu/ZnO/Al₂O₃ catalyst, including simultaneous formation of methyl esters and hydrocarbons." *Catalysis Today* 24 (1995 :) 5-14.

³⁸ Xiaolei Sun "Promoted Zinc Chromite Catalyst for Higher Alcohol Synthesis in a Slurry Reactor, Ph.D Thesis, North Carolina State University, 2001.

interesting updates to the status of commercialization given in the 2003 technical report is the decrease in interest by technology developers to further advance HAS technologies.

1.4.1 Snamprogetti (also referred to as SEHT – Snamprogetti, Enichem, and Haldor Topsoe)

In the 1980's Snamprogetti and Haldor Topsoe jointly developed a HAS process known as MAS (Metanolo piu Alcoli Superiori – methanol plus higher alcohols). The process was similar to a high pressure, high temperature methanol synthesis process, but the drawbacks of the modified methanol catalysts were supposedly avoided. They started a 12,000 tonne/yr pilot plant in 1982, and they sold the alcohol mixture as a 5 vol% blend in a gasoline called SUPER E.³⁹ Despite the initial interest and promise, the MAS process is no longer available from these companies for the production of mixed alcohols.⁴⁰

1.4.2 Dow

While Dow was one of the first to develop and advance HAS technology, Dow is no longer pursuing the commercial development of their mixed alcohols process. In 1997, they offered to sell their patents for their Sygmal mixed alcohol production process to Power Energy Fuels, Inc. (PEFI). PEFI did not buy the patents, and subsequently, the patents have expired. PEFI is currently attempting to commercialize a modified version of Dow's technology; Dow is no longer involved.

1.4.3 Lurgi

Lurgi developed their HAS process, known as OCTAMIX, with a low pressure methanol synthesis process in the 1980s and early 1990s. The process tended to yield higher alcohols, and 2 TPD demonstration plant was built in 1990. Lurgi indicated that they are no longer pursuing this technology; no detailed technical information is available.

1.4.4 Institut Francais de Petrole (IFP)

The latest development in IFP's commercial mixed alcohols process occurred in the late 1980's when they built their 20 BPD pilot plant in Chiba, Japan. Since that time, they have not ventured forth with any new units. In fact, according to their Strategic Marketing division, IFP has not further their work since they built

³⁹ G.A. Mills, and E.E. Ecklund, E.E. "Alternative Fuels – Progress and Prospects-2." Chemtech, 19, no.10 (1989): 626-631.

⁴⁰ Niels Udengaard, Haldor-Topsoe: Syngas Technology Group. May 4, 2005. Office Communication

the pilot plant, and they have no commercial interest in pursuing a mixed alcohols process.⁴¹

1.4.5 Ecalene™

The Ecalene™ mixed alcohol process continues to be developed by Power Energy Fuels, Inc, based in Lakewood, Colorado. The process is a modification of Dow's Sygmal process using its polysulfite catalyst. Currently, the process has not moved beyond the bench scale, and the planned 500 gallon/day pilot plant is no longer being pursued.⁴² However, there are 2-3 other pilot plants under funding consideration that would produce mixed alcohols from various biomass sources, such as tires, wood chips, and refused derived fuel (RDF). One of the pilot plants in consideration is a 2,000 gallon/day pilot plant at the Wabash River Coal Gasification facility in conjunction with ConocoPhillips. PEFI management predicts that the Ecalene™ process will be ready for commercialization in 2006, and will be able to produce 1 gallon of mixed alcohols per 270 SCF of syngas.

1.4.6 Envirolene™

The Standard Alcohol Company of America currently has a bench scale process to produce a mixed alcohols product known as Envirolene™. Envirolene™ is composed of methanol through octanol. Approximately 50% of the product is ethanol, but a more detailed breakdown of its composition is not available due to its proprietary nature⁴³. The process uses a modified high pressure methanol synthesis catalyst. The company is currently seeking funding for a pilot plant.

1.4.7 Pearson Technologies

Pearson Technologies has developed a 30-ton per day biomass gasification and alcohols conversion facility in Aberdeen, Mississippi. While both the gasifier and catalyst design are proprietary, it is believed that the catalyst is a modified FT catalyst formulated to selectively increase the production of ethanol. The overall Pearson design includes alcohol fractionation and recycle in an effort to purify the desired ethanol product⁴⁴.

⁴¹ Colin Baudouin, IFP Strategic Marketing. April 22, 2005, Office Communication.

⁴² Gene Jackson, Power Energy Fuels, Inc, President, April 21, 2005, Office Communication.

⁴³ Bob Dergay, Standard Alcohol Company Project Manager, April 29, 2005, Office Communication.

⁴⁴ Descriptions of this technology can be found at "The Manufacture of Synthetic Gas and Ethanol from Biomass using the Pearson Thermochemical Steam Reforming and Catalytic Conversion Process", Pearson, Stanley, presented at the 5th International Biomass Conference of the Americas, 2001, and "Gridley Ethanol Demonstration Project Utilizing Biomass Gasification Technology: Pilot Plant Gasifier and Syngas Conversion Testing", NREL/SR-510-37581, February 2005.

A project is currently 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. Funding for this project includes \$50MM raised from special purpose revenue bonds issued by the state⁴⁵. At the time of this report, it does not appear that a size or confirmed project timeline has been established.

1.5 Conclusions and Future Research Needs

Catalyst Selection

There is no one catalyst that is best suited for every mixed alcohol process design. A set of criteria to evaluate each catalyst should be developed, project developers must determine which of the criteria is most important, and finally, evaluation of the trade-offs should occur. The key criteria that should be used in each analysis are per-pass conversion, alcohol yield, product selectivity, operating conditions required, sensitivity to impurities, and cost. The performance criteria—conversion, yield, and selectivity—will be summarized here.

- **Conversion:** No one catalyst is clearly superior when it comes to per-pass conversion. Conversions are dependent on a number of factors, including catalyst formulation, doping agents, syngas impurities, and process conditions. Regardless of the catalyst chosen, recycle of anywhere from ~40 to 90% of the process stream will be necessary to maximize production of mixed alcohols.
- **Alcohol Yield:** Both modified methanol and molybdenum catalysts have shown higher alcohol yields than modified Fischer-Tropsch catalysts. The most recent research into process conditions, catalyst formulations, and metal promoters have shown that molybdenum catalysts can outperform modified methanol catalysts in this criteria under certain conditions.
- **Selectivity:** Molybdenum catalysts have shown superior performance for selection of higher alcohols over either modified methanol or Fischer-Tropsch catalysts. The relative benefit of this must be evaluated on an economic basis.

The tolerance of molybdenum catalysts to both sulfur and carbon dioxide give it another advantage over the other types of catalysts. These benefits must be weighed against process condition requirements, catalyst costs, and final product specifications to determine the catalyst appropriate for each design.

⁴⁵ Honolulu Star Bulletin, 23 June 2004, Star-Bulletin Staff. These bonds were originally authorized in 2000.

Future Research Needs

The data that is currently available for mixed alcohol synthesis is adequate to perform an overall systems analysis. However, a broad R&D program would be helpful to more accurately determine the best catalyst formulations for downstream product requirements. A comprehensive R&D program should include:

- Additional data gathering on clearly defined catalyst performance conditions to allow more direct comparisons between catalysts. The current literature available makes this type of comparison difficult due to different operating conditions, processes, and evaluation methods.
- A determination of catalyst sensitivities to other impurities that may exist in a biomass-derived syngas stream. This could include metals, halides, ammonia, heavy hydrocarbons, nitrogen, and others.
- Optimization of yields and selectivities for the desired product. For example, if use as a transportation fuel is desired, a set of specifications for the mixed alcohol product should be defined that is desired and compatible with this goal. Catalysts should then be optimized with these goals in mind.
- Greater investigations into reactor configurations and conditions to improve process performance.

2.1 Sulfur Removal Requirements and Options

The gas clean up issues for mixed alcohol synthesis processes fall into two different categories. The first category is for modified methanol and Fischer-Tropsch synthesis catalysts. Because the sulfur allowance for the modified catalysts is similar to the unmodified catalysts, the sulfur clean up issues will be the same. Sulfur limits are .1 ppmv and 60 ppb for the modified methanol and Fischer-Tropsch catalysts, respectively. The second category includes sulfide-based catalysts, such as MoS₂, that do not have the strict sulfur clean up requirements of the other catalysts. In fact, these catalysts may require relatively high levels of sulfur in the syngas in order to operate most efficiently. While these catalysts may not require significant syngas sulfur treating, the final product sulfur specification for use as a motor fuel or chemical blendstock may require additional sulfur removal.

2.1.1 Modified Methanol and Fischer-Tropsch Synthesis Catalysts

The sulfur removal technology chosen for syngas cleanup depends upon the sulfur removal requirement, the total amount of sulfur in the syngas, and the downstream process conditions. The modified catalysts for higher alcohol synthesis have the same sensitivity to sulfur in the syngas feed stream as the unmodified methanol and Fischer-Tropsch catalysts. Sulfur levels below .1 ppmv are preferred in order to avoid poisoning the methanol synthesis catalysts. Similarly, the Fischer-Tropsch synthesis catalysts can require sulfur levels as low as 60 ppb. All of these catalysts require very low levels sulfur that will dictate the use of a physical absorption unit or ZnO beds as a polishing step.

In general biomass to syngas cases, the total amount of sulfur to be removed is relatively small. Because the total amount of sulfur is likely to be under 20 TPD for even the largest plant, the most economic sulfur removal technology would most likely be the LO-CAT[®] process. The use of a physical (Selexol or Rectisol) or chemical (amine-based) solvent system would require a sulfur recovery unit, such as a LO-CAT[®] process or a CLAUS plant. LO-CAT[®] is used for small-scale applications with less than 20 TPD of sulfur to be removed, while a CLAUS plant is generally economic for large-scale applications with greater than 20 TPD. LO-CAT[®] can also be used independently to achieve 99.9%+ H₂S removal efficiency. Therefore, for sulfur removal applications of less than 20 TPD, a LO-CAT[®] unit followed by a ZnO adsorbent bed is recommended to achieve the necessary sulfur removal.

However, it is important to consider the CO₂ concentration of the syngas feed and recycle streams and the catalyst's sensitivity to CO₂. Small amounts of CO₂ in the syngas streams can have detrimental effects upon higher alcohol yields for modified methanol catalysts. Depending upon the catalyst's sensitivity to CO₂, it may be beneficial to use a physical or chemical solvent system that can remove CO₂ as well as sulfur to ensure the optimal syngas feed for a catalyst.⁴⁶ This would have to be decided by an economic analysis of additional capital costs for sulfur removal and the increase in mixed alcohol yield that can be attained.

If the total amount of sulfur in the syngas feed were to significantly increase (above 20 TPD) as a result of a different feedstock or a larger plant size, other technologies may become more economically reasonable. Sulfur removal technologies that could achieve the same levels of sulfur removal would be selected based upon the process conditions of the higher alcohol synthesis reactor. For instance, physical solvents might be favored over amine-based solvents, because physical solvents operate more effectively at higher pressure. The ZnO bed would still be required as a polishing step for Selexol with all catalysts, but it would only be required for Rectisol when used with the modified Fischer-Tropsch catalyst.

2.1.2 Sulfide-Based Catalysts

The nature of a sulfide-based catalyst changes the requirements for upstream sulfur removal. Sulfide-based catalysts are activated by the presence of sulfur in the syngas feed stream, particularly in the 50 – 100 ppm range.⁴⁷ Thus, upstream acid gas removal as extensive as the modified methanol and Fischer-Tropsch catalysts is not required. In fact, the Ecalene™ process being developed by Power Energy Fuels, Inc. claims that there is no need to do any upstream acid gas removal regardless of the origin of syngas.⁴⁸ Because the sulfur requirements in the syngas stream vary depending upon the type of sulfide-based catalyst used, two options for sulfur removal will be discussed.

2.1.2.1 Upstream Acid Gas Removal from Syngas

The first option to consider is removing sulfur in the syngas stream to the 50 – 100 ppm range. The base assumption for removal will be for a 2000 TPD biomass-fed gasification plant, using either direct or indirect gasification technology. The most economically justifiable sulfur removal technology would be the LO-CAT® process. Capable of achieving a 99.9%+ H₂S removal

⁴⁶ Dow and Union Carbide assumed the use of MDEA as a CO₂ removal process in their systems.

⁴⁷ P. Courty, et.al. (1990). "Production of methanol-higher alcohol mixtures from natural gas via syngas chemistry." *Revue de l'Institut Francais du Petrole*, 45, no.4 (1990): 561-78.

⁴⁸ Gene Jackson. PEFI – President. April 21, 2005. Office Communication.

efficiency, the LO-CAT[®] process could reduce the sulfur levels in the syngas feed to that required by the higher alcohol synthesis reactor. A physical or chemical solvent process is still not economically justifiable, because the total amount of sulfur removal required is less than 20 TPD. The most notable change between the sulfur removal technologies required by the modified catalyst and the sulfide-based catalysts is the lack of need for a ZnO bed; since no polishing step will be needed, costs can be reduced.

Reducing sulfur removal requirements will lead to some savings related to sulfur removal capital and operating costs, but it may not be as substantial or as beneficial as it first appears. First, there will be savings associated with a turned-down LO-CAT[®] process. In order to achieve a sulfur level of 50-100 ppm in the syngas, smaller equipment and less chelating agent would be used than required for a 99.9%+ H₂S removal. This would slightly decrease capital and operating costs, although it is not likely to be significant since capital must still be spent to install a LO-CAT[®] unit. Second, removal of the ZnO beds will not reduce capital costs significantly; the beds cost roughly 1/10th that of a LO-CAT[®] unit, and only made up 0.2% of the installed capital costs in the 2005 NREL Biomass to Hydrogen report (~\$350,000 in a \$152MM project).⁴⁹ Because the savings may not be significant to the overall cost of a plant, an economic analysis should be performed when comparing sulfur tolerant and non-tolerant catalysts based on incremental changes in cleanup requirements.

The second option to consider is to eliminate a sulfur removal unit altogether. If assured that sulfur levels in the syngas feed will not poison a sulfide-based catalyst, sulfur removal steps may be able to be eliminated. The benefits would come from the capital cost reduction and elimination of waste sulfur removal requirements. However, it is important to understand that some form of downstream product cleanup may be required if upstream syngas cleanup is not done. A project developer must also be sure that the feedstocks selected will never have high levels of sulfur if a design without sulfur cleanup is chosen.

The third option would be to do more extensive sulfur clean up in the syngas than required by the sulfide-based catalyst. This option arises from future federal sulfur specifications for gasoline that would not be met if there were no downstream sulfur removal. Choosing this cleanup option would depend upon an economic analysis comparing upstream acid gas and downstream sulfur removal costs. This option may actually be detrimental to sulfided catalysts that require some sulfur to operate most efficiently.

⁴⁹ Pamela Spath, et al. "Biomass Syngas to Hydrogen Production Design Report." National Renewable Energy Laboratory, January 31, 2005.

2.1.2.2 Downstream Sulfur Removal

The benefit of sulfide-based catalyst is avoiding some degree of syngas sulfur removal. However, because H₂S is not removed in its entirety, significant sulfur concentrations may be present in the mixed alcohols product. Regardless of if the end use of the product is for use as a transportation fuel or for chemical applications, it is likely that additional sulfur may need to be removed if this is not performed in the syngas stream.

The breakdown of sulfur species present in the mixed alcohols product could vary based on the feedstock and sulfur removal technology. Certain sulfur species, such as H₂S and mercaptans, can be a problem if not removed to extinction. These compounds are extremely corrosive and damaging to gasoline and diesel engines. Any H₂S would cause the gasoline to fail fungible gasoline specifications. Mercaptans can also be a problem depending on the regional regulation and standard. Thus, if these species are present in the mixed alcohols above allowable limits, either additional syngas sulfur removal or downstream sulfur cleanup will be required. The downstream product usage sulfur specification may reduce or eliminate any advantage that sulfided catalysts bring to the process.

If sulfur in the syngas stream remained above 30 ppm, downstream sulfur cleanup would be required to meet future national sulfur requirements for gasoline. The Environmental Protection Agency's Tier 2 Gasoline Sulfur requirements will phase in a 30 ppm sulfur limit by 2011 on gasoline.⁵⁰ The mixed alcohol blend would therefore have to have a sulfur level of 30 ppm or lower, with no H₂S, and very limited mercaptans. This would require one of two sulfur cleanup choices: either upstream acid gas removal from syngas, or removal of excess sulfur from the mixed alcohol product. An economic and catalyst performance analysis should be performed to determine the appropriate sulfur removal option.

When considering the type of catalysts to be used for HAS it will be important to identify the desired use for the mixed alcohols, the end product sulfur specifications, and the type of sulfur species present in the syngas. There is potential savings in eliminating sulfur removal units for sulfide-based catalysts, but this should be carefully evaluated versus product requirements and catalyst costs.

⁵⁰ Tier 2 Gasoline Sulfur Final Rule with Amendments. 8/29/02. available at http://www.npra.org/issues/fuels/pdf_gasoline.pdf

2.2 Summary and Conclusions

In order to choose the catalyst and appropriate sulfur cleanup technologies to meet design needs, an economic analysis should be done that will incorporate the following factors: desired mixed alcohol product slate, sulfur specifications, CO₂ removal requirements, and cost of sulfur removal.

- Desired alcohol product slate: The different catalysts for HAS have distinct conversion rates and yields for methanol, ethanol, isobutanol and other higher alcohols. A decision should be made considering what the desired composition of the final mixed alcohol product slate is before determining the sulfur cleanup required. However, it may still be possible that sacrificing some yield of a desired product could be compensated for by reduced cleanup costs.
- Sulfur specifications: NREL should follow the expected federal and state sulfur specifications for transportation fuels and chemical grade alcohols. If sulfur cleanup for product, not catalyst, requirements are necessary, an evaluation of the best way to perform this step should be made. This analysis should be compared against using catalysts that are not sulfur tolerant.
- CO₂ Removal: Because CO₂ can inhibit certain catalysts, particularly modified methanol synthesis catalysts, the right combination of CO₂ removal and H₂S removal should be explored. If CO₂ removal needs to be incorporated into a HAS process, more costly sulfur removal technologies may become necessary. This would provide extra incentive to use sulfur tolerant catalysts, since they are also more tolerant to high levels of CO₂.
- Sulfur Removal: Actual costs for the needed sulfur removal technologies should be developed. This would help with an overall economic analysis of what catalyst would be the most economically attractive and, thus, commercially viable.

3.1 Introduction

In general, a considerable amount of uncertainty and risk exists in the biomass to mixed alcohols process. Not only does the biomass gasification section of the plant have risk by itself, but unlike alternative syngas-to-liquids processes such as Fischer-Tropsch (FT), no commercial plants exist solely for the manufacture of mixed alcohols from syngas. The limited experience from both a feedstock conversion and product synthesis side creates a number of risks that must be considered when moving forward with a concentrated effort to make this technology a commercial reality.

This section will outline the major technical and economic considerations that should be addressed in order to progress the current state of the technology. Amongst the items that will be addressed include:

Technical Risk

- Feasibility of Producing the Desired Product Slate
- Scale-Up Considerations
- Reactor and Overall Unit Process Conditions
- Catalyst Sensitivities and Run Life

Economic Risk

- Competitiveness versus Petroleum Transportation Fuels
- Catalyst Manufacture and Prices
- Overall Process Economics for Gasification and Synthesis

Besides a literature survey and analysis of past Bechtel/Nexant reports, efforts were made to find analogies in similar technologies in determining the barriers that had to be overcome for commercialization. For example, in order for FT liquids production to be successful, commercial facilities must be able to find markets where FT from syngas has an advantage over petroleum based fuels. While this study is not a comprehensive marketing analysis, efforts have been made to identify potential solutions to mitigate some of the risk that this technology faces.

3.1.1 Drivers for Additional Research on Mixed Alcohols Synthesis

Due to the lack of large-scale production data, along with a number of outstanding questions and research areas for mixed alcohol synthesis from biomass, incentives and focus needs to be provided in order to place appropriate emphasis on this technology. This will help to provide a common basis for what needs to be accomplished to bring the technology to commercial fruition.

Definition of Research Needs

Currently, the available data for production routes, potential catalysts, and commercial application is fairly diverse, covering a wide range of areas. In order to progress the technology, a greater definition must be made for what the commercial use of the products will be. This will help to define what the catalyst yields, process set-up, and downstream refinement requirements are. Catalysts and technologies that are less promising for the eventual commercial use can be excluded from current consideration. Niche opportunities can also be identified at this stage in order to help establish the most attractive technologies to be pursued.

Policy Options

As with many other emerging technologies, research efforts can be spurred by government policy intervention. If biomass derived mixed alcohols had support from a concerted agricultural, security, and/or economic basis, focus could be placed on promotion of this technology. This support could come in the form of credits, such as the 51 cents/gallon ethanol credit, mandates, such as state renewable energy requirements, or focused research funding that would encourage additional research and development. While the appropriate policy tool is outside the scope of this analysis, consideration should be made of the options available to assist with technology promotion.

3.2 Technical Risk Analysis

A number of unanswered technical questions exist at this stage of mixed alcohol process research. The main items include the overall process feasibility to produce the desired product slate, the ability to scale-up the process to a commercial level, the appropriate process conditions both in the reactor and upstream units, performance of various catalysts at commercial conditions, catalyst sensitivities, and appropriate syngas compositions. After establishment of the desired product slate, each of these risk areas should be evaluated with prioritization placed on ways to reduce the inherent risk. This section will provide greater detail for the major areas of technical risk, and suggest ways to handle the risks involved.

Since NREL has been given the priority of exploring options for biomass derived fuels to displace petroleum, the assumption will be made that the end product desired is mixed alcohols as a transportation fuel. Each risk area will be analyzed with that priority in mind.

3.2.1 Feasibility

From a technical perspective, questions must be answered if catalysts are suitable to produce the product slate desired with reasonable performance characteristics (such as catalyst life, process efficiency, and once-through product yield). This is one of the few areas that has had considerable research performed. However, much of the research has only been performed on a bench-top level, with little optimization or tests under “real” industrial conditions. Key to answering this question is analysis of three areas: what product slate is desired, what catalysts are currently available or hold promise, and the impact that synthesis side products have on the downstream application.

Product Slates and Catalysts Available

When considering the optimum mixed alcohol slate that could be produced for use as a transportation fuel, the following items should be considered for their impact on the gasoline or diesel pool⁵¹. A more in-depth review of these items will be made in the Economic Risk section.

- Effect on Octane/Cetane Number
- Effect on fuel volatility: V/L ratio and Reid Vapor Pressure (RVP)
- Effect on fuel distillation curve
- “Enleanment” effect of mixed alcohols
- Effect on fuel economy
- Effect on water solubility and phase separation
- Effect on pool sulfur and aromatics content

These items should be prioritized based on the market where they are expected to be introduced. For example, in US markets that require reformulated gasoline, RVP and aromatics content are of greater concern than other fuels specifications. A general product slate can be theorized that is optimum given the transportation fuel constraints, and then catalysts chosen that best fit this desired slate. Many times, disconnects that exist between the desired product slate and the catalysts available will set research priorities.

In general, heavier alcohols (C3+) are superior to light alcohols (methanol and ethanol) on a number of these criteria. Heavier alcohols have better octane ratings, lower RVPs, a distillation curve more comparable to gasoline than light

⁵¹ Parts of this list are derived from a similar one established by Chandra Prakash, Motor Vehicles Emissions and Fuels Consultant, “Use of Higher Than 10 Volume Percent Ethanol/Gasoline Blends in Gasoline Powered Vehicles”, Environment Canada, November 1998.

alcohols, and superior energy content⁵². Focus should potentially be placed on catalysts that have higher yields of these types of alcohols. Another advantage of the higher alcohols are their ability to act as a co-solvent that allows methanol and ethanol to be blended in higher proportions without hitting pool constraints relative to these alcohols alone. Trade-off studies for catalysts producing different proportions of light versus heavy alcohols should be performed to determine the most promising catalyst for future research. Besides just considering the different product yields, downstream processing, such as fractionation of the light alcohols for other uses, should also be considered⁵³.

Side Products

Each catalyst has a unique quantity of side products (potentially up to 20%) that will be produced, which may either benefit or hinder the ability of the final product to be blended into transportation fuels. Compounds such as FT liquids and DME, have been identified as potential side products from mixed alcohol catalyst.

- FT Liquids, a potential co-product of cobalt-based catalysts, may be beneficial depending on the ratio of naphtha to diesel (the catalyst “alpha value”). While octane values may be impacted negatively, the resulting product would likely be heavier, leading to a lower volatility. As mentioned in Section 1, other hydrocarbons have also been witnessed from catalysts where the alkali-doping has been reduced. This side product will hurt product octane value, but will have a varying impact on other properties, depending on the carbon content of the hydrocarbon.
- DME is derived from Cu/ZrO₂ containing catalysts, and have been found to be less prevalent as CO₂ concentrations in the syngas decrease, while being more prevalent at higher reaction temperatures⁵⁴. This high cetane product is an excellent diesel fuel substitute, and could be advantageous to mixed alcohol blends depending on the downstream application.

An analysis of the downstream application for the mixed alcohol product will help to provide focus and determine what catalyst is best suited for the selected application. It is unlikely that one catalyst will be both technically feasible and optimized economically, which is why prioritization is key. Preliminary analysis would suggest that modified methanol catalysts containing copper might be less desirable due to the relatively high methanol yield. Modified FT catalysts

⁵² Information for part of this analysis provided by Smith and Workman, “Alcohol for Motor Fuels”, Colorado State University, 15 February 2005.

⁵³ Methanol was fractionated off the mixed alcohol product, vaporized, and used as fuel gas in one scenario of Fluor’s “Co-Production of Fuel Alcohols and Electricity via Refinery Coke Gasification”, Gasification Technologies 2003 Conference, San Francisco, October 2003.

⁵⁴ Klier and Herman, et. al., “Oxygenates via Synthesis Gas”, Lehigh University, as a subcontractor to Air Products and Chemicals, US DOE subcontract DE-FG22-95PC93052, April 1999.

containing cobalt could have superior performance depending on the downstream application. Molybdenum catalysts, which selectively produce high ethanol content products, are also beneficial due to their lower methanol yields.

One final feasibility consideration that should be made revolves around how policy will impact gasoline formulations. The product selected should take into consideration likely future fuels policy that may change requirements for oxygenates, RVP, aromatics, and sulfur, while also keeping in mind how current ethanol policy will influence mixed alcohols derived from biomass gasification. Mandates on ethanol blending may drive technical research toward higher ethanol, rather than heavier alcohol, yields. In addition, mixed alcohol fuel blends will need to be certified by appropriate federal and state agencies for blending into the motor fuel pool. Since two mixed alcohol products, from Lurgi's OCTAMIX and PEFI's Ecalene processes, have already been certified by the EPA, the technical hurdles to achieving certification should be limited.

3.2.2 Scale-Up

To varying extents, limited operational information exists on both biomass gasification operation and mixed alcohol synthesis on a commercial level. While analogies exist for the scale-up of other technologies, such as FT synthesis, it will be difficult to estimate with certainty the technical performance and economic impact of a commercial biomass to mixed alcohols plant. This is a risk inherent to any emerging energy technology.

Some performance data exists on pilot-level and small commercial size biomass gasification plants that can be used for scale-up purposes. Units such as those run in Scandinavia, Hawaii, and the Eastern United States may provide adequate information for scale-up purposes, as well as pilot scale facilities tested by a number of commercial vendors. In addition, larger gasification facilities have been built for coal and petroleum coke that can also provide performance and sizing data.

Additional technical risk comes in scaling-up a mixed alcohols reactor. Since little information on pilot or commercial scale performance exists, a testing program using either an existing gasifier or syngas derived from natural gas would help to provide important scaling data. In addition, analogies in processes such as FT synthesis, DME production, or other catalytic processes (such as COS or hydrotreating reactors), may be useful in estimating the major issues involved in scaling from the current plant sizes.

3.2.3 Process Conditions

The overall process conditions required for mixed alcohol synthesis represents another major technical risk to successful commercial operation. The high

temperatures and pressures required will not only place a severe strain on catalyst performance, but will also require careful engineering of compressors, reactors, piping, and containment vessels to assure robust performance. Engineering analysis must take these conditions, which may be unlike other gasification designs, into account in order to obtain the most realistic estimates of the process performance and cost.

Reactor Operating Conditions

The process conditions required for conversion of syngas to mixed alcohols are severe, even by alternative liquid product from syngas standards. While methanol and FT synthesis require reactor pressures in the 500 to 1200 psia range and temperatures from 300 to 500 degrees F, mixed alcohol synthesis usually operates at around 1800 psia and 700 degrees F, but can vary depending on the catalyst. These process conditions are necessary due to the low activity of the catalysts used.

Requiring this level of temperature and pressure will add cost due to the need to compress the syngas to a much higher degree, and from incorporation of materials necessary for operation at these conditions. Available software for performance and cost estimation may not always be suitable for pressure vessels of this thickness, requiring special estimates. While materials exist that should be able to handle the severe operating conditions, careful consideration should be made for what materials are appropriate, and how this will impact plant performance and cost.

As an initial example of the higher cost for mixed alcohol synthesis, a preliminary estimate of the additional cost that would be required to compress a biomass derived syngas stream to 1800 psia relative to 450 psia (appropriate for hydrogen and FT reactors) and 1160 psia (appropriate for methanol reactors) was made. This estimate shows a net plant increase of 5 to 10% total installed cost (TIC) using the NREL Biomass Syngas to Hydrogen design as a base case and two different estimation methods⁵⁵. The difference in horsepower can be seen in Table 6.

⁵⁵ TIC estimate of the compressor used in the NREL “Biomass Syngas to Hydrogen Production Design Report”, Spath P., et. al., January 2005, was used as the base. The increase in cost was estimated both using the NREL scaling factor and a HYSIS derived estimate for the increase in HP, along with Bechtel data on cost for refrigeration compressors at different HP loads.

<u>Compression Required</u>	<u>Horsepower (BHP)</u>
16 to 450 psia (for H ₂ /FT synthesis)	~35,000
396 to 1160 psia (for methanol synthesis)	~10,000
1160 to 1800 psia (for mixed alcohols)	~4,000

The lower compression ratio required as stream pressure increases reduces the marginal horsepower requirement. Please note that this estimate does not take into account the different pipe, flange, and downstream unit thicknesses required to handle the higher pressure. These additional costs to accommodate mixed alcohol synthesis represent another risk to future commercial application.

Catalyst Life

Due to the severe process conditions of higher alcohol synthesis, it would be expected that catalyst life would not be significantly long. As a benchmark, it could be helpful to recognize that the catalyst life for the typical Fe-Co Fischer-Tropsch catalyst can be longer than 5 years.⁵⁷ Information on catalyst life is not abundant because most research into HAS is bench scale and not commercial. However, the catalyst life data available does not demonstrate the longevity of the typical Fe-Co Fischer-Tropsch catalyst.

The majority of information available on catalyst life comes from the earlier commercialization attempts of different catalyst and processes in the 1980's. As an example, Dow and Union Carbide found the longest life for their MoS₂ catalyst to be in excess of 8 months (~5,700 hr), and at that time it retained 80% of its C₂+OH selectivity at a 20% CO conversion rate.⁵⁸ Also, Snamprogetti's MAS process demonstrated that their methanol-synthesis like catalyst has a catalyst life over 8,000 hr at temperatures between 626 – 806 °F.⁵⁹ Short catalyst life would produce high operating costs due to frequent replacement of the catalyst, and decreased performance during the relatively catalyst run life.

⁵⁶ The HYSIS model developed for the Nexant LP clean-up design case was used for the flowrate and composition.

⁵⁷ Energy Research Centre for the Netherlands. Biomass – Fischer-Tropsch Synthesis. Available at <http://www.ecn.nl/biomassa/research/poly/ftsynthesis.en.html>

⁵⁸ G. Quarderer, *ibid.*

⁵⁹ A. Paginni, D. Sanfilippo, D. "MAS Process: From Research to Commercialization". Paper presented at 78th Spring National AIChE Meeting. New Orleans, LA, April 1986.

Catalyst Activity

The amount of activity in mixed alcohols catalyst can vary widely based on a number of factors. This creates a significant technical design difficulty when estimating the per-pass conversion, the amount of recycle necessary, and the appropriate downstream treatment required. Activity and conversion will not be steady throughout the life of a catalyst, requiring designers to include considerable flexibility in plant designs.

Priority will have to be placed on catalyst activity relative to other items such as sensitivity to stream impurities and catalyst cost. Since each design will have a different set of criteria priorities, it is difficult to say at this time how this factor should be taken into consideration. It should be estimated with as much certainty as possible, with design factors included to keep activity stable and predictable.

Catalyst Sensitivities Other Than Sulfur

Impurities in the syngas that could impact mixed alcohol yield and selectivity are a major technical risk to successful plant operation. Catalyst sensitivities to sulfur were discussed at length in Section 2.1. Some impurities, such as CO₂ and water, have been researched specifically for their impact on mixed alcohols production, while the impact of others, such as metals, halides, ammonia, and nitrogen, can be predicted with some accuracy if modified methanol or FT catalysts are used. For catalysts with a more limited testing database, such as MoS₂, greater research should be performed to reduce the risk that a previously unknown poison will impact the process.

The impact of some of the potential stream impurities are listed below:

- Carbon Dioxide: In research performed by Lehigh University⁶⁰, it was found that increasing levels of CO₂ increase the product methanol yield for Cu/ZrO₂ catalysts. This is not surprising, for the fast reaction between CO₂ and H₂ over methanol catalysts is well known. As with methanol catalysts, high levels of CO₂ may be undesirable due to the lowered process efficiency and the impacts of higher methanol concentrations in the final mixed alcohol product.

However, as mentioned in Section 1.2.4, molybdenum catalysts are relatively tolerant to CO₂. The level of impurity tolerance will be very much dependent on the catalyst chosen.

- Water: Lehigh also found that increasing the water concentration would promote CO₂ production and decrease alcohol formation. Surprisingly, the higher CO₂ yield does not then produce proportionally higher amounts of

⁶⁰ Klier and Herman, *ibid.*

methanol, as what may be expected. If an amine scrubber is included after the mixed alcohol reactor in the recycle loop, the additional CO₂ will be removed, potentially reducing process efficiency. It is unlikely that syngas entering the synthesis reactor at 1800 psia will have water, making this impurity of reduced interest.

Little other research on the impact that water has on other catalyst types exists.

- **Known FT and Methanol Catalyst Poisons:** Metals, halides, ammonia, and nitrogen all act to reduce catalyst activity and catalyst life. As with other syngas to FT and methanol designs, steps should be made to reduce these impurities if modified FT or methanol catalysts are used. A greater level of testing should be performed to determine if the sensitivity to these poisons are as great as with straight FT or methanol catalysts.

Hydrogen to Carbon Monoxide Ratio

Depending on the alcohol product slate desired and the type of catalyst used, the appropriate ratio will vary. Whatever ratio chosen should be strictly maintained to optimize process performance. In general, a lower ratio has been found to be better for higher alcohol synthesis, as the table below shows:

Table 7: Stoichiometric H₂/CO Ratio, Different Alcohols	
<u>Product</u>	<u>Stoichiometric Ratio</u>
Methanol	2.0
FT Liquids	2.0
Ethanol	1.0
Propanol	0.8
Butanol	0.71

In the 2003 Fluor/Ecalene co-production study⁶¹, a 1:1 ratio was applied, while the 1996 Bechtel study⁶² used a lower ratio (0.5 to 0.7) to promote more C4 alcohol production for MTBE synthesis. Maintaining this ratio will be more challenging in a plant with full recycle, while a limited recycle plant with either purge or co-production will run less risk of unoptimized product yields.

Depending on the feedstock and gasification process, efforts may be necessary to reduce the H₂/CO ratio in the syngas stream in order to promote heavy alcohol

⁶¹ Fluor 2003 Gasification Technologies Conference paper, *ibid*.

⁶² “Economics of MTBE via Mixed Alcohol Synthesis”, as a subcontractor to Air Products US DOE Study *Alternative Fuels and Chemicals from Synthesis Gas*, cooperative agreement DE-FC22-95PC93052.

production. This is especially true in biomass gasification systems. The main options that should be considered for reducing this ratio include:

1. Pressure Swing Absorption (PSA) to remove hydrogen. While this step would be easiest to control relative to other options, a use for the pure hydrogen stream must be found and incorporated into the design.
2. Unreacted CO recycle. Some degree of recycle will occur in all mixed alcohol designs. The type of catalyst chosen and desired product slate will greatly impact how the recycle will impact the inlet reactor stream composition.
3. Injection of CO₂ into the tar cracker. If a relatively pure CO₂ stream is removed from the process, introduction of CO₂ into the tar cracker may promote a reverse water-gas shift, increasing the CO concentration. The amount of CO₂ and type of tar cracking catalyst will dictate the amount of extra CO that will be produced from this process.
4. Minimizing steam injection into the gasifier. Since excess steam may cause unnecessary hydrogen production, efforts should be made to eliminate steam injection beyond what is required for fluidization or thermal control. Testing of both steam injection into the gasifier and CO₂ injection into the tar cracker should be performed to determine how these efforts would impact the ratio.

The appropriate design to reduce the ratio is very dependent on the mixed alcohol catalyst chosen, the desired product slate, the gasifier technology used, the feedstock selected, and other process steps. Each design case must be uniquely evaluated to determine the preferred method for producing the desired H₂/CO ratio.

3.3 Economic Risk Analysis

Besides the obvious impact that mixed alcohol synthesis has on process design economics, the other major areas of economic risk are the competitiveness of the mixed alcohols product versus petroleum based transportation fuels and the risk inherent to new catalyst formulations. This section will elaborate on the major economic risks in the process, and suggest areas for future study and research.

Once the externalities of petroleum based fuels are taken into consideration, policy makers may find that pursuing mixed alcohols from biomass as a motor fuel is an attractive option. In fact, some states have already started to take action in this area. California Assembly Bill AB2076 mandates that the California Energy Commission explore efforts to “reduce petroleum dependence” in motor fuels, which has been interpreted as an effort to pursue alternative transport fuels. States such as New York, Massachusetts, New Jersey, Connecticut, Rhode Island, Vermont, and California have also enacted some form of low, ultra

low, or zero emission vehicle programs that, depending on the policy structure, may also stimulate the use of alternative fuels. These sorts of efforts, coupled with potential tax incentives, may be the driving force that stimulates additional work in this field.

3.3.1 Comparison with Petroleum Based Transportation Fuels

If the key use of mixed alcohols from syngas is as a replacement for petroleum based fuels, a direct evaluation of the advantages, disadvantages, and compatibility with the current fuels infrastructure is necessary. This analysis would determine what economic drivers exist for application of the fuel, and what roadblocks must be overcome to incorporate mixed alcohols into the fuels system.

Price

At least two comprehensive studies have evaluated the economics of producing alcohols from petroleum coke—a 1996 Bechtel study specific to MTBE production with C1 and C4 alcohols as an intermediate, and a 2003 Fluor/Ecalene study for co-production of mixed alcohols and electricity. Both studies were mentioned in the technical risk section of this paper. A comparison of the two cases is shown below:

Table 8: Mixed Alcohol Economic Study Comparisons		
	<u>Bechtel (1996)</u>	<u>Fluor/Ecalene (2003)</u>
Product(s)	MTBE from C1/C4 alcohols	Ethanol, Propanol, and Power
Feed Rate (Pet Coke)	1800 TPD	4758 TPD
Feed Cost	\$0/ton	\$0/ton
Plant Cost	\$350-400MM	estimated at >\$1 billion ⁶³
Product Value	\$0.85 cents/gal MTBE	\$1.15 cents/gal for alcohols, 4.4 cents/kWh power
Return on Investment	~13%	~15%

The entries from these studies were placed in the Nexant IGCC Financial Model⁶⁴ in order to test key study sensitivities and competitiveness of the

⁶³ Details of plant cost were not provided in the Fluor study. This estimate is derived from the Nexant IGCC Financial Model, using the inputs and output flowrates, along with estimated feedstock and product values shown by Fluor.

products versus petroleum fuels. Assuming the alcohols produced are used for fuels blending and not either MTBE production or for chemicals value, taking into account the lower energy content of mixed alcohols relative to gasoline, and assuming that this level of return is acceptable to investors, these studies show mixed alcohols to be competitive with gasoline at a wholesale value of \$1.25 to \$1.70 a gallon, depending on the cases being evaluated.

Two unevaluated items in these studies could swing the economics considerably. One is the assumption of the feedstock cost. While petroleum coke may be ample and low cost for gasification applications, it is unclear if this would be the case with biomass. Sensitivity analysis performed by Nexant at \$30 and \$50/ton feedstock cost, making assumptions for general plant inputs not covered by the studies, show that the price of gasoline would have to rise by 20-25% in the \$30/ton case and 30-40% in the \$50/ton case for the pet coke based alcohols to be competitive. The other unevaluated input is the application of a production credit like that levied to ethanol (51 cents/gallon). A credit of this nature could swing the plant economics of an unattractive investment to very attractive if the full credit could be realized.

While a complete design and economic analysis is outside the scope of this evaluation, projecting these plant economics to a biomass based system gives perspective to the economic hurdle that must be overcome for biomass to mixed alcohols plants to be pursued commercially.

Blending

Blending mixed alcohols into existing gasoline and diesel pools will be beneficial for some fuels specifications and detrimental to others. Mixed alcohol blending will be similar in impacts to ethanol blending for many gasoline specifications. The key specifications that will be impacted were mentioned in Section 3.2.1. Impacts on octane, volatility, sulfur, aromatics, and corrosivity will be elaborated upon here.

- **Octane:** Mixed alcohols provide a considerable octane boost to petroleum gasoline pools, with octane values generally rising as the carbon content increases. Some commercial marketers of mixed alcohol for fuels use market their fuels with octane values of over 120 or 130⁶⁵. Mixed alcohols would be of considerable benefit in octane-constrained markets.
- **Volatility:** Although the RVP of neat alcohols is lower than gasoline, when blended in small amounts (5 to 25%), alcohols have a negative impact on

⁶⁴ Nexant, Inc. developed the ICGG Financial Model Version 3 for the US DOE, National Renewable Energy Laboratory, under a task order from E²S, Subcontract Agreement No. 7000002220, 2003.

⁶⁵ Power Energy Fuels, Inc. markets their Ecalene product as 124 octane, while Standard Alcohol Company of America, Inc. claims an octane rating of 138.

pool RVP⁶⁶. Lighter alcohols adversely impact pool RVPs more, but the presence of heavier alcohols act as a “co-solvent” for light alcohols, allowing higher levels of light alcohols to be blended relative to blending them neat. For model purposes, commercially available mixed alcohols are marketed as blending like ethanol for volatility purposes⁶⁷.

- Sulfur and Aromatics: The tightening of fuels specification throughout the world has recently led to demands for lower sulfur and aromatics content fuels. Since mixed alcohols would largely be free of or very low on both accounts (although sulfur may be higher in sulfur tolerant catalysts, an issue dealt with in Section 2), mixed alcohols produced in this fashion could be beneficial to meeting lower targets for both these specifications.
- Corrosivity: Depending on the level of alcohols blended, the type of alcohols, and the amount of phase separation that occurs, alcohols have been found to be corrosive to certain materials used in engines⁶⁸. In general, higher blends and lighter alcohols create more corrosive environments. Based on the formulation that is created, modifications to vehicles may need to be performed, adding to the economic hurdles that must be overcome to widely use mixed alcohol fuels.

A number of studies have evaluated the economic impact on both fuels markets and federal economies from the addition of ethanol to fuel pools. A similar analysis should be performed with mixed alcohols, based on the expected product make-up, to determine the level of economic risk that wider commercial application will have.

Transport and Storage

Special issues have arisen in transporting and storing methanol and ethanol for transportation fuels applications. Due to their limited solubility in gasoline in the presence of small quantities of water, pipeline transport rarely occurs, and special consideration must be made for the storage of alcohol/gasoline blends. Only 1-2% water can be tolerated in 25-40% alcohol mixtures, with the tolerance decreasing as the alcohol content decreases⁶⁹. Water making its way into storage tanks has led to phase separation and corrosive environments.

⁶⁶ Volatility information provided by Meridian Corporation, “Properties of Alcohol Transportation Fuels”, prepared for the Biofuels Systems Division of the US DOE, July 1991.

⁶⁷ Testimony by Mark Radosevich, Standard Alcohol Company of America, in front of the California Environmental Policy Council, January 18, 2000.

⁶⁸ Smith and Workman, *ibid*.

⁶⁹ Meridian Corporation, *ibid*.

Fortunately, the presence of higher alcohols acts as effective co-solvent for lighter alcohols such as methanol and ethanol. Mixed alcohol blends that have sufficient quantities of these higher alcohols may be less susceptible to transport and storage problems that neat methanol and ethanol face. Greater analysis of the proposed fuel for blending should be performed to gauge the level of risk.

3.3.2 Catalyst Prices

Depending on the catalyst chosen to perform mixed alcohols synthesis, the price of the metals that go into the catalyst production will impact the cost of the production route to some extent. While this is less important for more common metals such as copper and zinc, exotics such as molybdenum, cesium, and rhodium prices may make certain synthesis routes cost prohibitive. An analysis of the metals that will go into the desired catalyst for mixed alcohols production will provide insight into the level of economic risk involved. A list of the metals considered for application, their prices, alternative uses, and risk level are shown below.

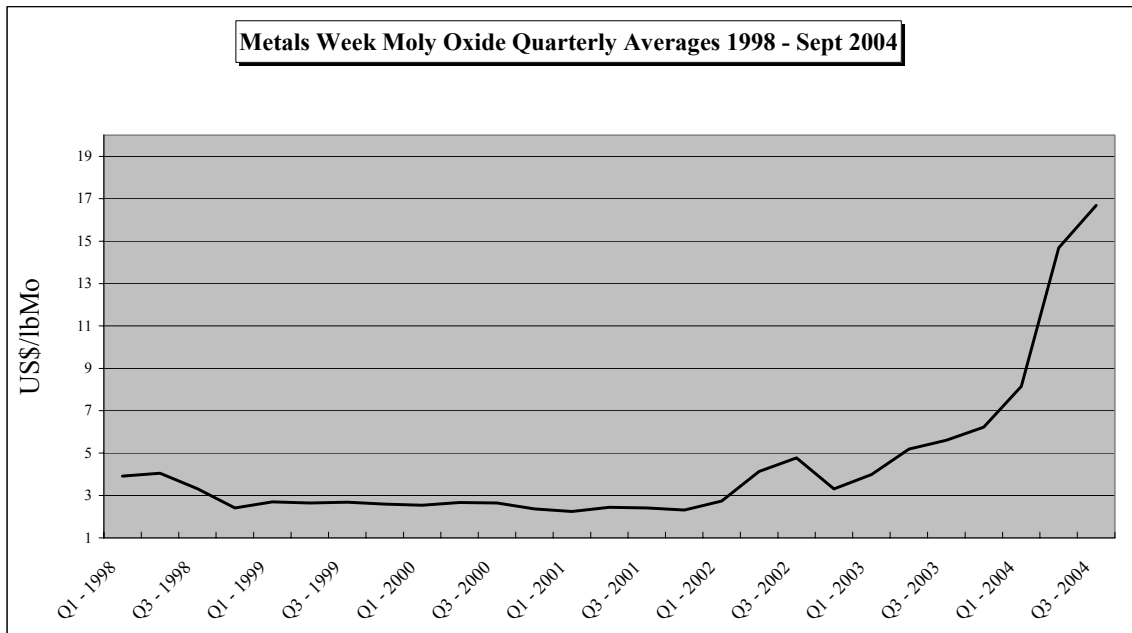
Table 9: Metals Considered for Use in Mixed Alcohol Catalysis			
<u>Metal</u>	<u>Price⁷⁰</u>	<u>Other Uses</u>	<u>Risk Level</u>
Molybdenum	\$2 to 40/lb	Steel alloys; price tracks well with steel price	Moderate
Rhodium	\$600 to 1800/ounce	Turbine engines, electric connections	High
Copper	\$1 to 2/lb	Major industrial metal; electricity and telecom	Low
Chromium	\$3 to 6/lb	Steel and nonferrous alloys	Low
Zinc	\$0.30 to 0.60/lb	Major industrial metal; iron and steel coating, alloys	Low
Cobalt	\$20 to 40/lb	Gas turbine superalloys, steel	Moderate
Cesium	\$30 to 60/gram	Specialty chemical, medical, & electrical apps.	Very High

Less common industrial metals that are considered for mixed alcohols synthesis bring an extra level of economic risk to the catalysis operation. For example, molybdenum's major industrial application, as an alloying element in steels and cast irons, can lead to a high level of volatility based on the demand for these

⁷⁰ The range presented is from a number of sources, looking at the current market and volatility over the past 10 years.

products. This was witnessed in 2004 when world steel demand pushed molybdenum prices to \$35/lb, a 1300% increase from 2002⁷¹. A graph of the recent trends in molybdenum oxide prices, which track closely with the metals price, can be seen in Figure 1.

Figure 1: Molybdenum Oxide Prices, 1998 to 2004⁷²



Other factors such as the cost and activity of support materials (alumina oxides and activated carbon), and the complexity of mass production of this catalyst, creates economic risk that must be better understood.

3.3.3 Process Economics

Building upon what was mentioned in the technical risk section, the overall process to convert biomass feedstock to mixed alcohols carried a significant amount of economic risk. The considerable uncertainty in developing cost estimates for a process with no current commercial application must be reflected by adding contingency factors to the overall process, with a special process contingency placed on the mixed alcohol synthesis unit. While much of the plant process cost can be estimated from other biomass gasification facilities, unique considerations and design requirements for a mixed alcohol facility adds additional cost and risk.

⁷¹ Dave Forest, Casey Research LLC, March 2005.

⁷² From the International Molybdenum Association, www.imoa.info, London, UK.

Contingency Estimates

The major areas of economic risk in a biomass to mixed alcohol facility are from the gasification unit, syngas cleanup costs, purification and fractionation of alcohols (if required), and stream recycle with carbon dioxide removal. In addition, uncertainty exists around how the mixed alcohol synthesis unit will perform, making estimates for economic purposes difficult. Contingency estimates outlined below are based upon DOE's "Quality Guidelines for Energy Systems Studies"⁷³, which provides a consistent basis for evaluating energy technologies.

- **Gasification Plant:** As mentioned earlier, biomass gasification itself is not a mature technology. Reliability of the gasifier is key to long run lengths and attractive plant economics. **Process contingency = 25%**
- **Cleanup Costs:** Much of the technology used in syngas cleanup, such as particulate removal, sulfur extraction, reforming, and water quench/scrubbing has a number of industrial applications. Special technologies, such as warm sulfur removal and advanced tar cracking catalysts, may require higher contingencies if used in this application.
Process contingency = 15% for commercially proven technologies, higher for advanced ones.

During the cleanup stage of the process, the syngas will need to be compressed and heated to the mixed alcohol reactor conditions. The severe conditions, coupled with the swings between hot gas exiting the gasifier, cooling for treatment, then reheating for reactor requirements, creates additional cost and higher levels of economic risk. These conditions will require a cleanup section more expensive than typical for biomass systems.

- **Alcohol Purification and Fractionation:** Depending on the catalyst selectivity and the products desired, a purification or fractionation step may be required downstream of the reactor. As this is a mature technology, little risk is added, but this step represents a cost unseen in most gasification plants.
Process contingency = 5%, yet costs are added to the plant that may increase the TIC by 1 to 5%.
- **Recycle and CO₂ removal:** Due to low once-through conversion, the unreacted syngas will need to be recycled back to the reactor in plants where mixed alcohols are the main product. This recycled stream must be treated, likely with a CO₂ removal step, in order to maintain a constant

⁷³ "Quality Guidelines for Energy Systems Studies", Gilbert McGurl, et.al., Office of Systems and Policy Support, US DOE, National Energy Technology Laboratory, January 2005.

H₂:CO ratio in the reactor inlet. The design of this plant section must take into account contingencies for different H₂:CO ratios in the fresh feed, and the impact of different conversion in the reactor as the catalyst ages.

Process contingency = 15%, since CO₂ removal is fairly mature, yet additional capacity should be designed into the recycle loop to handle the range of process conditions that will likely occur.

- Reactor Design: The uncertainty in performance of this high pressure, high temperature reactor will require significant contingency built into the cost estimate. While assumptions can be made for conversions and yields throughout the lifetime of the plant, additional data should be gathered to confirm these assumptions. **Process contingency = 40%+**

Conversion Optimization

A number of steps can be taken, based on the catalyst and desired products chosen in the design, to modify reaction conversion. These include:

- Changes in the H₂:CO ratio
- Level of stream impurities
- Level of unconverted syngas recycle
- Co-products desired and plant flexibility
- Number of gasification, cleanup, and conversion trains

The impact that these changes have on the process economics should be evaluated to determine the best scenario for each plant design. The 1996 Bechtel study looked at a number of different per-pass and total conversion assumptions for both systems integrated with a refinery and as a stand-alone plant. For the integrated facility, they found an optimum total syngas conversion at around 51%. Above this conversion rate, the costs of recycling, due to larger reactor requirements, multiple trains, and recycle compression, outweighed the benefit of additional alcohol production. For the stand-alone facility, increasing per-pass conversions generally improved the plant economics.

3.4 Summary and Conclusions

In order to advance research and assist in commercial promotion, better definition for how the product will be used and what the long-term goal of the design effort is will be critical to developing an integrated analysis approach. Once these definitions are set, more focus can be placed on the appropriate catalyst to use, design conditions to meet goal targets, how the product can be integrated into the market, and what policy options can be used to assist in technology promotion. A clear R&D effort can then be developed to minimize and prioritize the inherent technical and economic risks.

Recommendations for technical R&D focus were made in Section 1.5. From the process side, a complete systems analysis should be performed to provide a preliminary basis for overall design requirements and costs. Once the systems analysis is complete, a plan should be established to demonstrate greater commercial feasibility. Part of this work can be accomplished along side the technical and economic systems analysis work:

- Testing of pilot scale reactors on syngas (can be derived from natural gas).
- Incorporation of pilot scale reactors with functioning gasifiers. Ideally, biomass derived syngas should be used, but data from coal and coke gasifiers will also be useful to the design process.
- Establish economic and policy drivers to promote commercial use of biomass to mixed alcohol technology. These may include alternative fuel credits, mandates to replace petroleum based fuels, or incentives to build and run biomass gasifiers.
- A greater analysis of the impact that the mixed alcohol product will have on the gasoline and diesel pools. May be able to use some of the information in the ethanol literature as a starting point.

NREL will play key roles in all stages of the development of mixed alcohol technology from biomass. The following are the main items that NREL should focus on at this stage and in the near future:

- Definition of the product use and appropriate process conditions
- Conceptual design and cost estimates for commercial mixed alcohol plants. The contingencies listed in the economic risk section should be used to provide the best estimate of the technology cost at this time. The systems analysis in this area should cover a range of sensitivities:
 - Different biomass feedstock types
 - Different catalysts, assuming advances in technology, that can help to set research drivers and goals
 - Different plant sizes
 - Different product uses, including chemicals, fuels, and power. Should consider co-production scenarios that could improve plant economics.
- Different R&D paths should be established based on the different product uses. The R&D paths would define what catalysts are most appropriate for each product, and what research needs to be focused on to enhance the current technology.

- Market analysis to determine feedstock availability, impact of mixed alcohol product on fuels and chemicals markets, and potential niche opportunities.

Finally, although outside of NREL's likely scope, a policy analysis of the most appropriate options to assist in technology advancement would be very useful along side technical and economic analysis. The policy analysis would help to determine how R&D funding could be promoted within the current system, and how the economics of the process could potentially be impacted by federal or state policies.

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