Final Scientific/Technical Report

Project Title: Biomass-derived Syngas Utilization for Fuels and Chemicals

Award Number: DE-FG36-GO85006

Recipient: RTI International
Project Location: Research Triangle Park, NC 27709

Project director/Principal investigator: David C. Dayton

Teaming member: W.R. Grace

Executive Summary

The growing gap between petroleum production and demand, mounting environmental concerns, and increasing fuel prices have stimulated intense interest in research and development (R&D) of alternative fuels, both synthetic and bio-derived. Currently, the most technically defined thermochemical route for producing alternative fuels from lignocellulosic biomass involves gasification/reforming of biomass to produce syngas (carbon monoxide [CO] + hydrogen [H_2]), followed by syngas cleaning, Fischer-Tropsch synthesis (FTS) or mixed alcohol synthesis, and some product upgrading via hydroprocessing or separation. A detailed techno-economic analysis of this type of process has recently been published [1] and it highlights the need for technical breakthroughs and technology demonstration for gas cleanup and fuel synthesis. The latter two technical barrier areas contribute 40% of the total thermochemical ethanol cost and 70% of the production cost, if feedstock costs are factored out. Developing and validating technologies that reduce the capital and operating costs of these unit operations will greatly reduce the risk for commercializing integrated biomass gasification/fuel synthesis processes for biofuel production.

The objective of this project is to develop and demonstrate new catalysts and catalytic processes that can efficiently convert biomass-derived syngas into diesel fuel and C_2-C_4 alcohols. The goal is to improve the economics of the processes by improving the catalytic activity and product selectivity, which could lead to commercialization.

The project was divided into 4 tasks:

Task 1: Reactor Systems: Construction of three reactor systems was a project milestone. Construction of a fixed-bed microreactor (FBR), a continuous stirred tank reactor (CSTR), and a slurry bubble column reactor (SBCR) were completed to meet this milestone.

Task 2: Iron Fischer-Tropsch (FT) Catalyst: An attrition resistant iron FT catalyst will be developed and tested.

Task 3: Chemical Synthesis: Promising process routes will be identified for synthesis of selected chemicals from biomass-derived syngas. A project milestone was to select promising mixed alcohol catalysts and screen productivity and performance in a fixed bed micro-reactor using bottled syngas. This milestone was successfully completed in collaboration withour catalyst development partner.

Task 4: Modeling, Engineering Evaluation, and Commercial Assessment: Mass and energy balances of conceptual commercial embodiment for FT and chemical synthesis were completed.

Publication:

Subramani V., Gangwal S.K. “A review of recent literature to search for an efficient catalytic process for the conversion of syngas to ethanol.” ENERGY & FUELS, Vol. 22(2), pp. 814-839.

A through review of recent literature on syngas to ethanol was prepared. More then 220 publications and patents were reviewed. The review looked at various routes and chemistries of

converting syngas to ethanol. Thermodynamic calculations were also presented to understand the limits on various reactions as a function of process parameters. Past research efforts in developing catalysts and reactor designs were extensively discussed to finally summarize the R&D needs in commercializing syngas conversion to ethanol.

Presentations:

"Evaluation of a Long-term Fischer-Tropsch Test and the Resulting Spent Iron Catalyst", Santosh K. Gangwal, Velu Subramani, and David A. Green, for presentation at the Houston AICHE meeting, April 2007

Contributions to the workshop "Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels", held in Washington, DC on June 25-26, 2007.

Technologies/Techniques :

New bench- and laboratory-scale reactors were developed for screening novel fuel synthesis catalyst formulations and conducting long-term catalyst performance tests.

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Introduction

The President's Advanced Energy Initiative (2006) calls for a change in the way Americans fuel their vehicles to promote improved energy security. Increasing biofuels production from domestic lignocellulosic resources requires advanced technology development to achieve the aggressive targets set forth recently by the President to reduce motor gasoline consumption by 20% in 10 years. A large fraction of the targeted 35 billion gallons of alternative fuels must come from sustainable biomass resources to minimize environmental impact and help to decelerate the impact of fossil fuels on global climate change. The U.S. Department of Energy (USDOE) Office of the Biomass Program (OBP) is actively funding research and development in both biochemical and thermochemical conversion technologies to accelerate the deployment of biofuels technologies in the near future to meet the goals of the Advanced Energy Initiative.

Thermochemical conversion technology options include both gasification and pyrolysis to enable the developing lignocellulosic biorefineries and maximize the biomass resource utilization for production of biofuels. Moving forward, the role of thermochemical conversion is to provide a technology option for improving the economic viability of the developing bioenergy industry by converting the faction of the biomass resources that are not amenable to biochemical conversion technologies into liquid transportation fuels.

Biomass gasification integrated with gas cleanup and fuel synthesis has emerged as the nearer term technology option for thermochemical biofuels production primarily because ethanol can be produced via mixed alcohol synthesis. The acceptance of non-ethanol biofuels is increasing as accelerated biofuels production is sought for increasing energy security and mitigating climate change and compatibility with the existing fuel distribution and infrastructure is becoming more of a technical challenge as the volume of biofuels production increases. Given the shear magnitude of the challenge of reducing gasoline consumption by 20% in 10 years (35 billion gallons of renewable and alternative fuels plus 5% increase in vehicle efficiency), alternative transportation fuels such as coal to liquids (CTL) is also being considered but the environmental concerns have quelled interest compared to biofuels even though economies of scale and CO_2 sequestration can improve the image of CTL.

Given the large volume targets established for biofuels production, mixed alcohol production from syngas (~90 gal/ton – comparable with fermentation) has received more interest than FT diesel (~50 gal/ton) for largely political reasons – ethanol is an accepted gasoline additive that gets the tax credit and the passenger car fleet predominantly uses gasoline, not diesel. These arguments do not hold for overseas possibilities for biofuels where FT diesel has a much stronger position to help meet EU biofuels goals. Other options like dimethyl ether (DME) that can be produced in high yields from syngas - via methanol conversion and dehydration – are also being considered as a diesel substitute and LPG alternative.

Ethanol from syngas has proved to be an economically competitive route for biofuels production. Feedstocks targeted for thermochemical conversion include forest and wood products residues and lignin-rich residues from the cellulosic ethanol process. Municipal Solid Wastes (non-recyclable consumer wastes and construction/demolition materials) are again being considered for thermochemical process because of the anticipated negative costs (tipping fees) and continuous resource availability. An interesting potential "energy" crop resource is pulp wood in the Southeastern US. The declining pulp and paper industry coupled with the inability to effectively use softwoods in a fermentation process make these forest resources an attractive feedstock for biofuel production.

The production of mixed alcohols from syngas has been known since the beginning of the last century; however, the commercial success of mixed alcohol synthesis has been limited by poor selectivity and low product yields. Single pass yields are on the order of 10% syngas conversion to alcohols with methanol typically being the most abundant alcohol produced [2, 3]. Methanol can be recycled to produce higher alcohols or removed and sold separately. One of the major hurdles to overcome before HAS becomes an economic commercial process is improved catalysts that increase the productivity and selectivity to higher alcohols [4]. To date modified methanol and modified FT catalysts have been more effective in the production of mixed alcohols; the sulfide-based catalysts tend to be less active than the oxide-based catalysts [2, 3].

The capital cost breakdown for these systems is 50% for syngas production, 29% for mixed alcohol synthesis, 17% for CO_2 removal, and 4% for product fractionation [5]. Economies of scale would improve overall process economics and opportunities also exist for cost reductions with improved catalyst yield and selectivity and better process integration to reduce energy losses. These technical and economic barriers to the commercialization of this technology need to be addressed by research and development efforts aimed at demonstrating integrated biomass gasification, gas cleanup and conditioning, and high-pressure catalytic synthesis of mixed alcohols.

The objective of this project is to develop and demonstrate new catalysts and catalytic processes that can efficiently convert biomass-derived syngas into diesel fuel and C_2-C_4 alcohols. The goal is to improve the economics of the processes by improving the catalytic activity and product selectivity, which could lead to commercialization. To achieve these goals, the performance of the RTI-6 FT catalyst will be optimized for utilization in a slurry bubble column reactor (SBCR) by extensive laboratory testing. For the synthesis of higher alcohols, economically viable routes will be identified and stable and selective catalysts will be tested.

The project was divided into 4 major tasks that was originally to be carried out over a 24 month period. This schedule has been delayed with the loss of our original cost share partner, Eastman Chemical and the addition of WR Grace as our new cost-share partner. Task 1 involved construction and commissioning of reactor systems. Task 2 involved development of an attrition-resistant iron-based FT catalyst. Task 3 involved development of selective catalysts for the synthesis of C_2 to C_4 alcohols. Modeling, engineering evaluation and commercial assessment of the catalytic processes developed were performed in Task 4.

Task 1: Construction and Commissioning of Reactor Systems

The objective of this task was to design, fabricate and install reactor systems suitable for the rapid screening of catalysts developed for the higher alcohol synthesis and Fischer-Tropsch (FT) synthesis of diesel fuel.

Subtask 1.1: Fixed bed high pressure micro-reactor

A fixed-bed high pressure micro-reactor system that can operate up to 1400 psi and 400^{o}C was to be used for the rapid screening of the catalysts developed for the higher alcohol synthesis. Such a high-pressure computer-controlled microreactor system was ordered from In-situ Research, Inc. (ISRI). This reactor system is capable of operating at 1400 psig and 400°C. A schematic diagram of the microreactor is shown in Figure 1. Upon receiving the high pressure computer-controlled mircroreactor system, it was leak checked with nitrogen at 500 psig. The heating jackets, thermocouples and temperature control system were tested, and minor repairs were made. This microreactor system was to be used for C_2-C_4 alcohol synthesis experiments.

Several modifications were made to the system to meet the desired requirements. Soft seated valves from heated zones of the saturator and reactor were removed. A liquid inlet port was added to the upstream end of the preheater.

Valves were added to the reactant gas supply lines to permit selection of different catalyst activation gas mixtures and different synthesis gas mixtures to be directed to the mass flow controllers. A porous metal disk of 316 stainless steel, 1/2 inch in diameter and 1/8 inch thick with a 40 micron nominal pore size was used as the catalyst support. A Swagelok fitting at the bottom of the reactor was machined to accommodate the porous disk catalyst support. The condenser was replaced with a sampling cylinder which was externally wrapped with 1/8-inch copper tubing which was connected to a chilled water system. The condenser was hydrostatically tested at 1100 psig. Provisions for draining the condenser include an accumulator of 1/4-inch tubing, isolated by a ball valve and a metering valve. A capillary gas chromatograph with mass spectrometry detector (GC/MS) was installed and calibrated to analyze the reactor effluents. A split stream of gaseous products and unconverted reactants was directed to this dual detector gas chromatograph for intermittent analysis. A heated orifice and heated transfer line was added to the gas sampling system to provide a hot near atmospheric pressure gas stream from the reactor exit to a sampling loop for the GC/MS. The output of this loop, after condensation of liquid products, was routed to the GC/FID-TCD to provide an ambient temperature sample for permanent gas analysis.

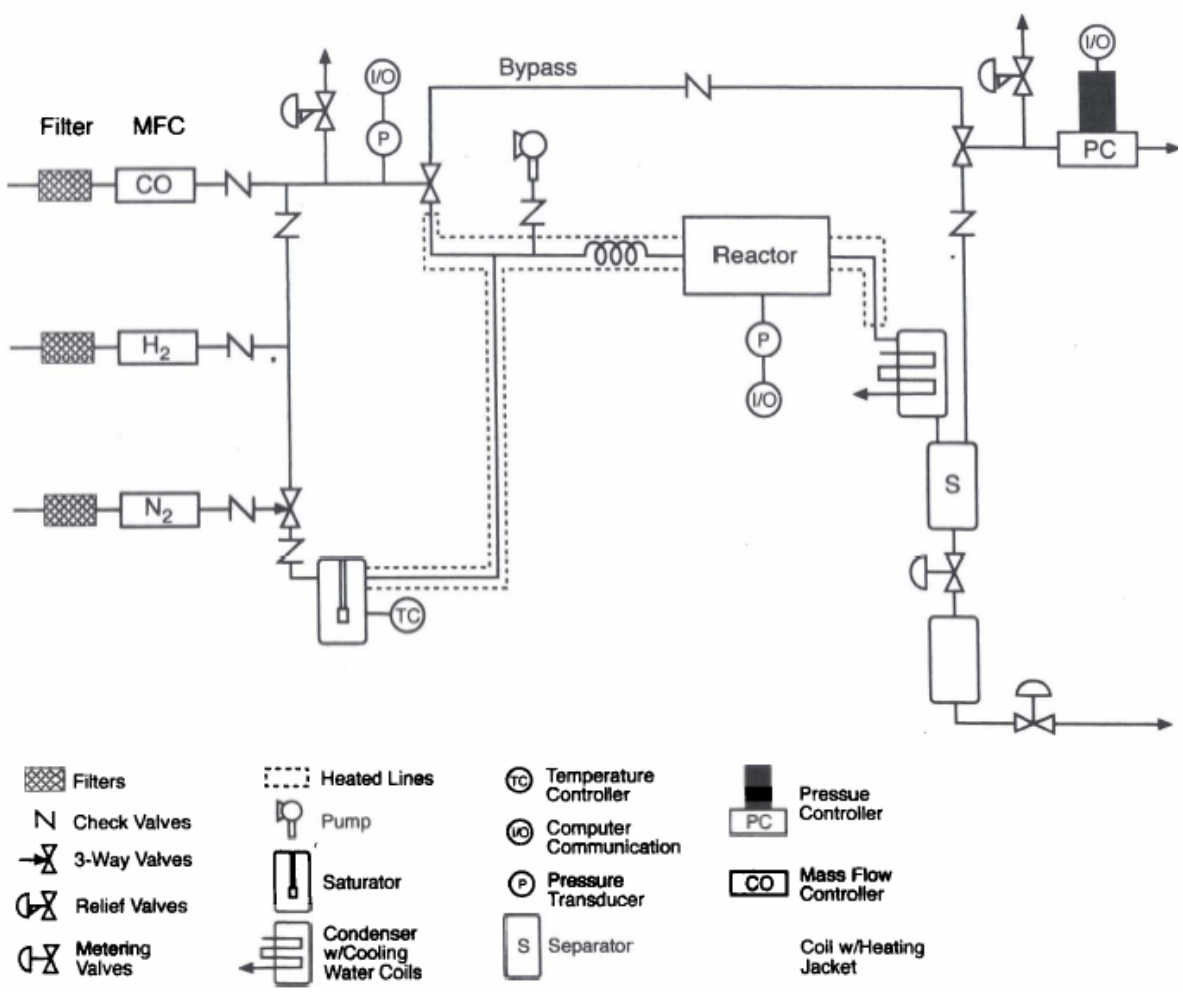

Figure 1. Schematic of Microreactor System

Subtask 1.2: Continuous Stirred Tank Reactor (CSTR)

Reactor set-up

A pre-existing Fischer-Tropsch Continuous Stirred Tank Reactor (CSTR) system at RTI was modified for use at higher pressures and temperatures. This modified CSTR system was used to screen FT catalysts. The reactant and purge gas delivery and conditioning system and the reactor are shown in Figure 2. The reactor and product and byproduct collection system is shown in Figure 3. The chemical analysis system is shown in Figure 4. A vacuum pump was used to move a split stream of the cooled reactor exit gas through a sampling loop for intermittent injection to the gas chromatograph. A Carle 400 gas chromatograph (GC) was configured for analysis of product gases. The GC has both a flame ionization detector (FID) and thermal conductivity detector (TCD). By using multiple columns and valve switching sequences, the FT product gas were analyzed for hydrogen, carbon monoxide, carbon dioxide, methane, C_2-C_5 alkanes, C_2-C_5 alkenes, and C_6^+ hydrocarbons by column backflushing. The molecular sieve columns in the GC were reactivated by conditioning at 300°C for four hours with a helium

purge. Reactivation was necessary to improve the separation of methane and carbon monoxide. An Agilent Technolgies GC ChemStation data acquisition system was configured for processing of the chromatographic signals from the Carle 400 GC.

After a test run of 300 hours, it was determined that uninterrupted operation was needed to avoid catalyst exposure to changing environment and thus avoid its deactivation. In order to develop this capability of operating the CSTR unattended, several safety features were introduced in the system and modifications to the data acquisition and control aspects were made.

A pre-existing reactor furnace temperature controller was replaced with a programmable controller capable of ramped heating and has a high limit signal which will shut down and lock out the power to all the heaters. A control for a high/high limit on the furnace temperature, a high limit on the reactor temperature and a high limit on the reactor pressure that would shut down and lock out the power to all of the heaters was developed. To continuously record all the system parameters, even during unattended operation, data acquisition system was developed to record the reactor temperature, furnace temperature, temperature of the first trap, reactor pressure using a transducer and two channels of mass flow meter/controller output. The two existing mass flow controllers were plumbed to control either 1) two separate reactant gases, or 2) a single premixed reactant gas plus purge nitrogen for sampling. A flow limiting valve was added to the reactant gas line. An additional pressure gauge was added to the system to permit monitoring of the pressure downstream of the reactor.

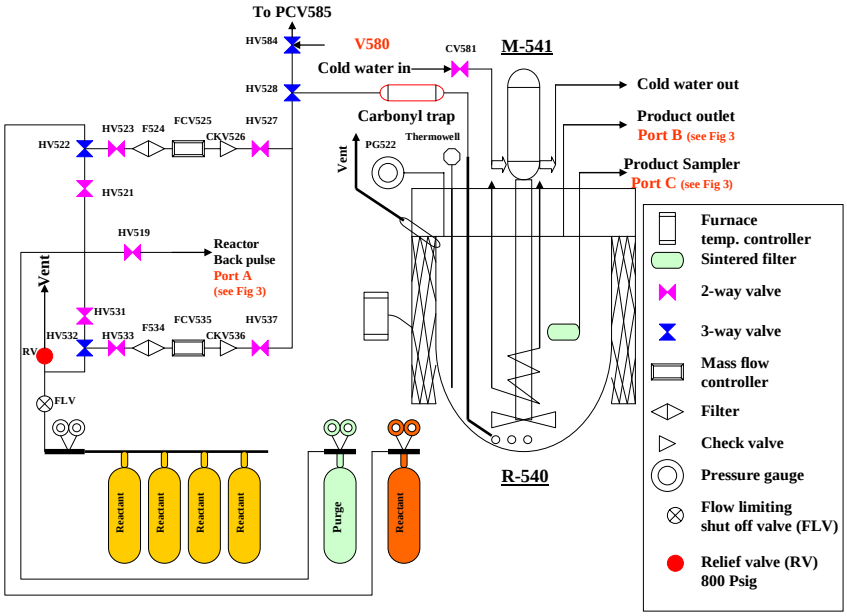

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Figure 2. Schematic of CSTR with Reactant Gas Metering and Conditioning System.

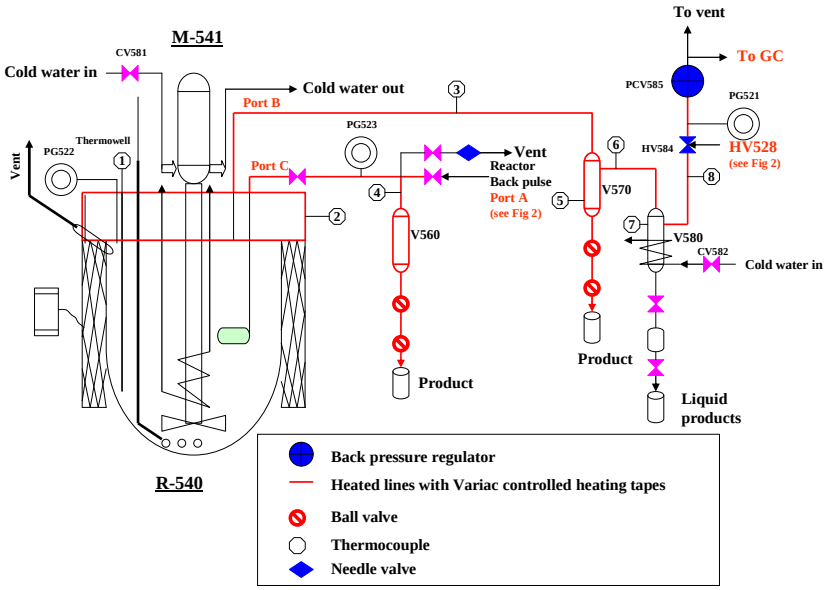

Figure 3. Schematic of CSTR with Product and Byproduct Collection and Sampling System.

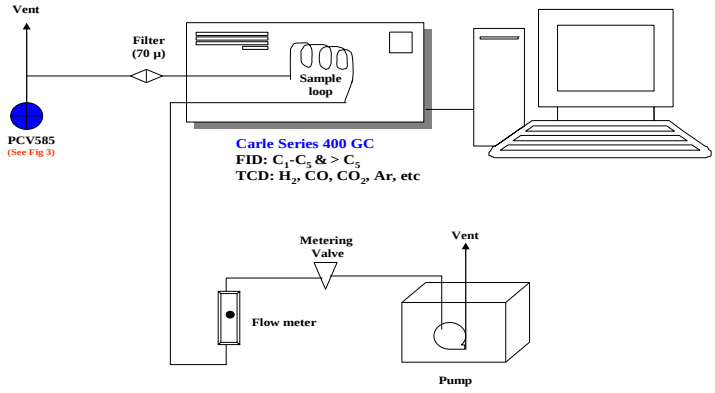

Figure 4. Schematic of In-line Gas Chromatographic Analysis System.

Subtask 1.3: Slurry Bubble Column Reactor (SBCR)

The Slurry Bubble Column Reactor (SBCR) is a 6' length of 1.25" Schedule 80 316/316L pipe and is shown in Figure 5. A process flow diagram of the reactor system is shown in Figure 6. . The details of reactor and product recovery system are shown in Figure 7. At the top of this 6' section, the pipe is expanded from 1.25" to 2" using a 1.25 x 1.50 and a 1.50 x 2.0 reducer. By rapidly expanding the reactor diameter, the velocity of the three phase mixture is rapidly

decreased. Under these conditions, the weight of the catalyst particles is greater than the lift of the moving liquid/gas mixture and the catalysts settles out of the mixture and falls back into the reactor.

The bottom of the reactor is sealed with a pipe cap; a fitting welded to this cap is fitted with a threaded plug which can be removed if it is necessary to drain the reactor. Premixed, preheated contaminant-free synthesis gas (molar $CO:H_2$ ratio is approximately 2:1) is added near the bottom of the reactor through a 1/4" tube. The gas mixture will also contain argon, which as a conservative tracer will be used to calculate total conversion by analysis of the exit gas composition in comparison to the reactor feed composition. This will eliminate the need to measure the volumetric flow rate of the gas exiting the reactor. This tube is cut off at a 45° angle on the end that protrudes into the reactor. Six 1/8" Type K thermocouples are inserted through fittings welded to the side of the reactor. These thermocouples extend to the inner wall of the reactor but do not protrude into the reactor.

The top of the reactor is sealed with a slip-on flange welded to the 2" section of pipe and a blind flange. The flange includes taps for bored through fittings to accommodate a cooling water loop of 1/8" 316 SS tube which extends approximately 3 feet into the reactor. Cooling water will be pumped through this loop, as needed, at near atmospheric pressure to extract heat from the reactor generated by the FT reactions.

A 1" pipe is welded to the 2" expansion section at the top of the reactor; a mixture of gas and liquid products (possibly containing some carried over catalyst solids) exits the reactor through this pipe. This pipe contains a tee; the branch of the tee provides a connection for a rupture disk fitting, the outlet of which is vented through a 1/2" tube leading to an open surge tank constructed from a 3" carbon steel pipe which is capped at the bottom and open at the top. The top of the surge tank will be at least 7 feet above floor level so that after any liquid product and catalyst is disengaged, gases will be discharged into laboratory exhaust above. The surge tank will be securely attached to the support frame on which the rest of the system is mounted. The run of the tee leads to the first product trap, which is maintained at 130ºC. This trap acts as a simple liquid/gas separator. This trap consists of a 1 foot length of 2" pipe flanged at the top and capped at the bottom. The liquid products can be periodically drained through a double ball valve arrangement connected to the cap at the bottom of the trap. Because a reduction in velocity of the three-phase mixture is the only active means of separating the catalysts from the liquid/gas products, some carryover of the catalyst from the SBCR in the liquid/gas effluent is expected.

Figure 5. Slurry Bubble Column Reactor and Product Traps

The gaseous effluent (with the possibility of some entrained liquids) flows from an elbow on the upper flange of the first trap to a water-cooled counter flow condenser. The saturated products from this cooler flow into a second trap maintained at room temperature and any additional condensed liquids are separated from the gas. The second trap is constructed of a 2 foot length of 2" pipe flanged at the top and capped at the bottom. The liquid products can be periodically drained through a double ball valve arrangement connected to the cap at the bottom of the trap. Gas flows from the second trap to a back pressure regulator. A majority of the effluent from the back pressure regulator is vented through the standard high flow exhaust ventilation system with a small slipstream being sent to a gas chromatograph for analysis.

Reactant gases (H_2, CO and/or premixed CO/H_2 which may contain an Ar tracer) and purge gas (N_2) are supplied from high pressure cylinders and controlled with mass flow controllers. The reactant gas is preheated before entering the bottom of the reactor in a heating coil maintained at a fixed temperature in a temperature controlled furnace. The reactor is heated with six independently controlled band heaters. The first trap is maintained at 130ºC with a band heater. The heated sections of the SBCR system are insulated to help maintain fixed temperature set points and protect personnel from contact with hot surfaces.

The slipstream of the gas effluent from the process is periodically injected into a chromatograph which is programmed to conduct a GC Chemstation method for analysis of the H_2, CO, and light hydrocarbon products. Liquid samples will be periodically drained from the traps and subjected to off-line chromatographic analysis.

Assumptions for RTI reactor design:

Assumptions for RTI Reactor		
Height	6	ft
Reactor ID	1.25	in
Reactor Temperature	260	deg C
Reactor Pressure	350	psig
Particle Density	1.3	g/cc
Wax Density	0.67	g/cc
Particle Size Range	45 to 90	micron
Average Particle Size	60	micron
Gas to Oil conversion	20	%

Following the work of Marretto, et al (1999), a catalyst volume fraction of 30% has been assumed. This is regarded as a conservative assumption: the syngas conversion increases with increased catalyst loading, however beyond a 40% catalyst volume fraction it may be difficult to retain the catalyst in the reactor.

Maretto, et al. determined from cold flow modeling (using paraffin oil with no solids) that the reference small bubble holdup, $\varepsilon_{df,ref}$ was 0.27 and the reference rise velocity for small bubbles, $V_{small,ref}$ was 0.095 m/s. The small bubble holdup, ε_{df}, is calculated:

$$\varepsilon_{df} = \varepsilon_{df,ref} \frac{(1-0.7\varepsilon_s)}{\varepsilon_{df,ref}} = 0.06$$

where the catalyst volume fraction,

$\varepsilon_s = 0.3$.

The small bubble rise velocity, V_{small} is then calculated,

$$V_{small} = V_{small,ref}(1+\frac{0.8\varepsilon_s}{V_{small,ref}}).$$

V_{small} = 0.305 m/s.

The small bubble superficial velocity, U_{df} is calculated as,

$U_{df} = (\varepsilon_{df})(V_{small})$ = 0.0183 m/s.

The big bubble holdup, ε_b, is based on the correlation of Krishna et al. (1997), as cited by Marretto et al,

$$\varepsilon_b = 0.3(\frac{1}{D_T^{0.18}})(\frac{1}{(U-U_{df})^{0.22}})(U-U_{df})^{0.8}$$

where D_T = the column diameter, 0.0381 m

U = the overall superficial velocity, 0.0443 m/sec

Thus, $\varepsilon_b = 0.0651$.

Then the total gas holdup in the system, ε is calculated as,

$\varepsilon = \varepsilon_b + \varepsilon_{df} (1-\varepsilon_b) = 0.121$.

In summary, the reactor will contain 12% bubbles, and 30% of the 88% non-bubble volume (26%) catalyst and the balance (that is, 62%) wax.

The superficial syngas velocity used in the University of Kentucky research reactor (Davis and Iglesia, 2001) was 3 cm/sec. For a 1.25 inch reactor system, this corresponds to 30 ft^3/hr. For operation at 300 psig, with a syngas composed of 1/3 H_2 and 2/3 CO (molecular weight = 19.3), this corresponds to approximately 34 lb/hr of reactant gas. Assuming that 20% of this is converted to liquid products, the reaction would produce about 1 gal/hr. Using a different approach, the assumed conditions of the Rentech system were extrapolated to a 1.25 inch reactor to be operated at 350 psig and 240°C. Under these conditions, a syngas flow rate of 28 SLPM corresponds to a superficial velocity of 4.4 cm/sec. If a 20% conversion of syngas to liquid products is obtained, about 2.5 gallons/day of wax would be produced.

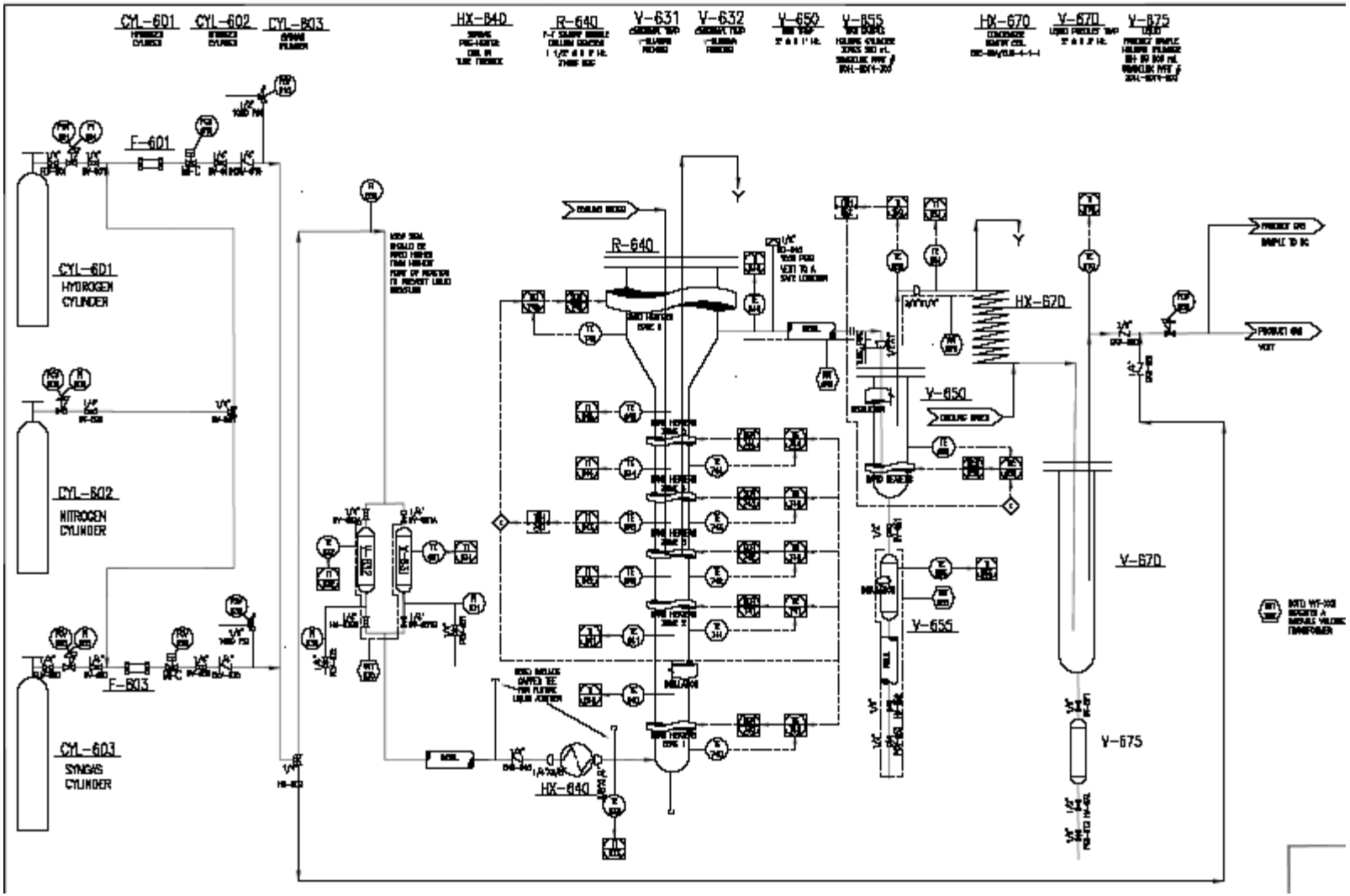

Figure 6: Process flow diagram of the slurry bubble column reactor

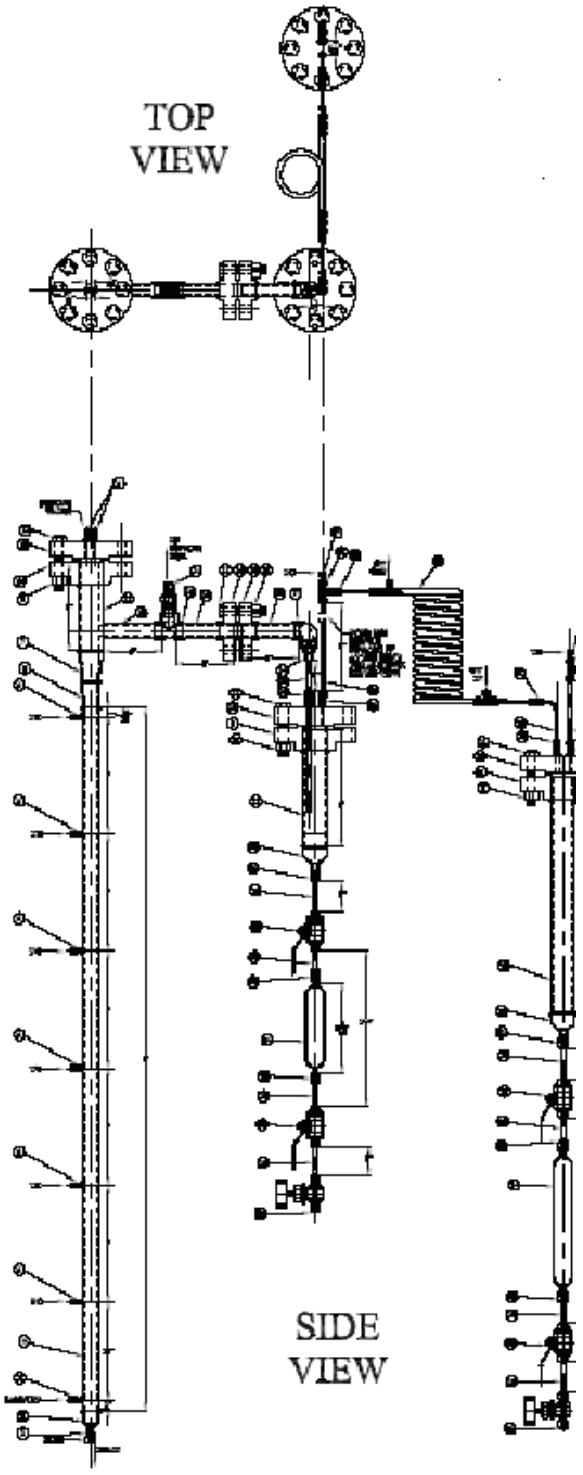

Figure 7. Details of Reactor and Product/Byproduct Recovery System

Subtask 1.4: Fixed bed high pressure micro-reactor for higher alcohol synthesis

Reactor set-up

A dual microreactor system was designed and fabricated for the purpose of testing mixed alcohol synthesis catalysts. The process flow diagram for the system is shown in Figure 8. After finalizing the operating ranges for the test parameters, the selection, sizing, and ordering of appropriate flow and pressure control components (e.g., control valves, check valves, meters/gauges, etc.) and heating equipment was completed. Construction of the system included a feed gas blending section to incorporate the components of the simulated syngas before it entered the microreactors. The second part of the system was the reactor section and included all flow, temperature, and pressure components. Lastly, product sampling for the microreactor system included a condensing section to collect all liquid produced and a gas chromatograph that provided on-line analysis of the gas components.

The simulated syngas feed was blended using hydrogen, hydrogen sulfide, and carbon monoxide to a composition per the test requirements. Brooks 5850i mass flow controllers (MFC) were used for flow rate control, and a Brooks 5860i mass flow meter (MFM) was installed upstream of the microreactor to verify the total gas flow through the system. A Brookes 0154i microprocessor based read out and control unit was utilized for the MFCs and MFMs. The CO feed gas was heated prior to entering the system by flowing the gas through a heated pressure vessel filled with alumina. Pressure control was achieved with a Tescom 2600 Series back pressure regulator rated from 0 to 1500 psig. Gas pressure was monitored upstream of the microreactor vessels using a properly sized gauge. To ensure the safety of the system, feed gas lines were equipped with flow limiting valves and check valves were used as well as pressure relief valves that were installed in any section that could be valved off from the system outlet.

The microreactor vessels were installed in parallel, and each reactor consisted of a ½" stainless steel tube containing a frit in the outlet fitting to contain the catalyst sample. To maintain the process temperature, the microreactors were fitted with two Wattlow Thinband 200W band heaters on a copper sleeve and fiberglass insulation to ensure even heating of the sample. For temperature sensing and control, a thermocouple well was installed to house a probe in the center of the loaded catalyst sample to measure the actual process gas temperature. The band heater control loop used a FUJI PXW-4 temperature controller to relay information based on the thermocouple probe. The tubing connecting the microreactor with the condensing vessel was heated with a ½" heat tape controlled with a Variac variable transformer. A surface thermocouple monitored the wall temperature of the process line.

The liquid collection system downstream of the microreactors consisted of a condensing vessel and cooling coil. The condensing vessel, a stainless steel 150 ml sized high pressure vessel, was chilled by wrapping a copper tube cooling coil around the vessel which continually ran cooling water maintained at 13 °C. The gas exiting these vessels was evaluated during the testing with a Carle Series 400 AGC gas chromatograph calibrated for H_2, N_2, CO, Ar, CO_2, and hydrocarbons including up to C_5. Online gas stream analysis allowed for constant monitoring of the reaction during testing. All liquid was collected at the end of the testing period and evaluated in an Agilent Technologies 5975C gas chromatograph / mass spectrometer.

Mixed Alcohol Catalyst Testing Protocol

Space velocity – 500 sccm/min for 10 cc of catalyst
100ppm H_2S in syngas mixture to maintain sulfidity
H_2/CO = 1.0 - 1.2
Space velocity ~ 4000/hr
Experimental Temperature Range 300 – 350°C (400°C upper limit)
Operating pressure – 900-1000 psi
GC analysis of permanent gases
Collect all liquid condensate in sample trap and analyze with GC/MS for alcohols, etc.
Use Ar as internal standard for mass closure calculations

Testing procedure

Catalyst testing in the microreactor starts with a compact bulk density measurement to calculate the required loading amount for 1000 hr^{-1} space velocity test condition. The catalyst sample is loaded into the reactor with a 1.5 dilution of the sample with ER-120 spheres. There are two reactors in the system, and both are loaded prior to any testing. Once the samples are loaded into the reactor set up, it is pressure tested to 1200 psig and held for 3 hrs to ensure a 0 psig leak rate. The samples are then subjected to a pre-defined sulfiding procedure simultaneously.

Catalyst testing is performed individually over a two day period. The following description uses process conditions from a previous test, but the pressure, temperature, and H_2/CO ratio can be adjusted to client needs. The pressure in the system is brought to 800-900 psig with pure H_2. At this point, the test flows are set at 60 sccm CO, 71 sccm H_2, and 0.01 sccm H_2S, which corresponds to a 1.2 H_2/CO ratio and 1500 ppm H_2S in the feed gas. The system is then brought to 1000 psig test pressure. As the system is brought to the correct pressure, the temperature is set to 325 °C on the temperature controller. When the system pressure and temperature are stable, the Carle 5 GC program is started to do online gas analysis of the permanent gases leaving the reactor system. The reactor system is monitored throughout the day to ensure the proper test conditions are maintained. During the test, any condensables are collected in a chilled water cooled vessel downstream of the reactor vessel. The chilled water is maintained by facilities and maintenance at ~ 13 °C. At the completion of the testing period, the GC program is stopped, and the liquid condensables are collected in a sample bottle for further testing. The pressure and temperature are brought to ambient conditions, and the reaction vessel is purged with nitrogen to ensure safe removal of the vessel.

Data from the GC analysis is collected for the entire testing period. The liquid sample is analyzed using a Mass Spectrometer to evaluate the components of the sample. These values are put into a data analysis spreadsheet to report the CO_2 free selectivities and performance of the catalyst sample.

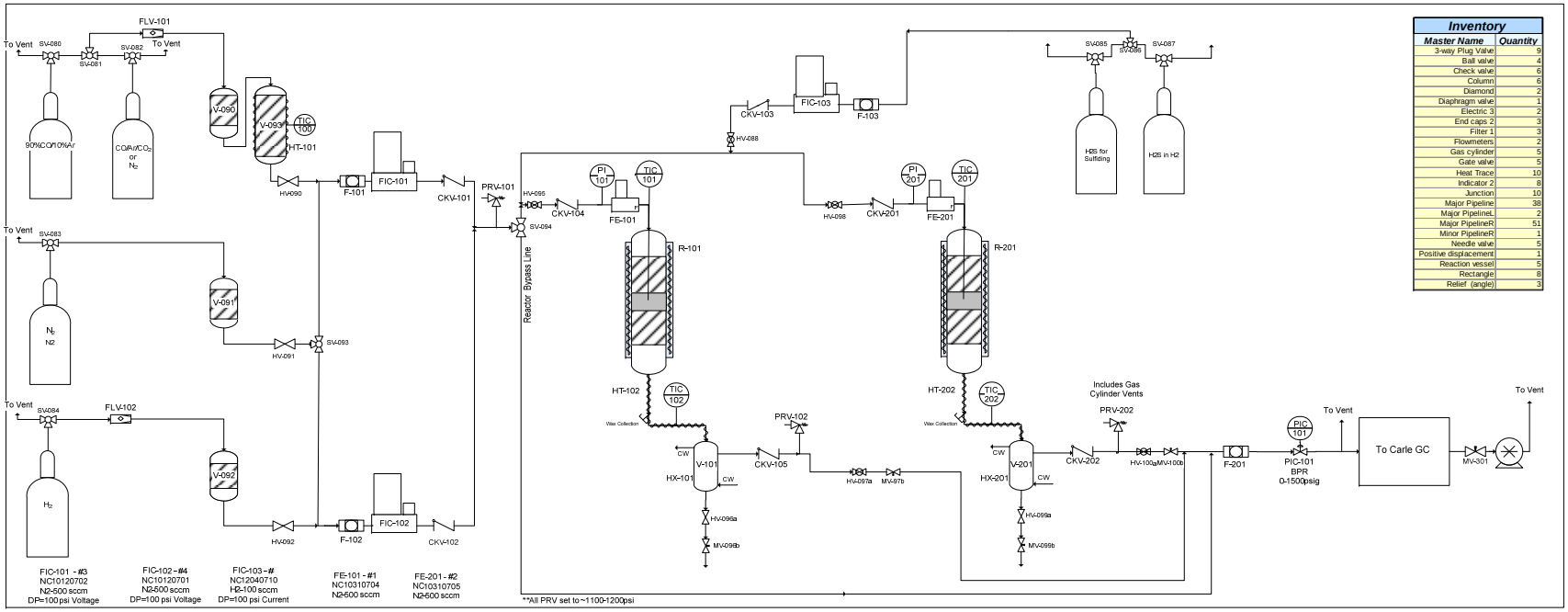

Figure 8. P&ID of the higher alcohol synthesis microreactor

Task 2: Testing of an Attrition-resistant Iron-based (Fischer-Tropsch) FT Catalyst

The main objective of this task was to perform the Fischer-Tropsch experiment for extended time periods using catalyst RTI-6, RTI's proprietary attrition-resistant iron based FT catalyst. The standard operating procedure used for all the experiments is discussed in the earlier section. The CSTR was charged with 150 g of wax (C_{25} to C_{34}) and 10 g of RTI's RTI-6 iron-based catalyst. A premixed synthetic syngas containing 55% CO, 38.5% H_2, and 6.5% Ar was used for all the experiments. The argon in the syngas served as an internal standard so that conversion of gases to liquid products could be readily determined based on the Ar concentration of the gaseous fraction of the reactor effluent. All tests were conducted at a space velocity of 2.2 SLPH/cc catalyst. In the initial part of the project, during unattended operation, synthesis gas was replaced with high purity nitrogen due to safety considerations. Nitrogen was replaced with synthetic syngas after re-start. Because of the time lag required for the reactor to return to steady state, the last sample of the day prior to switching the gas flow to nitrogen was used as the best indicator of expected performance in a continuously fed system. Following are specific results of this testing.

Preliminary extended time testing of RTI-6

A preliminary test to analyze the effect of longer on-stream time on the performance of catalyst RTI-6 for FT reactions was performed. For this purpose, the system was operated between March 10, 2006 and June 12, 2006. Data obtained during this test is plotted from Figure 9 through Figure 15. During this reaction, synthetic syngas flow as switched to pure nitrogen during unattended periods for safety considerations. When gas flow was discontinued, retained liquid (wax) product was removed.

Based on an argon balance the cooled reactor effluent gas flow rate was determined and the extent of CO conversion was calculated. Figure 9 through Figure 11 show the unconverted CO and the fractional conversion of CO to CO_2 and CH_4. Other gas phase organics present in the reactor effluent were also determined chromatographically. Concentrations of various compounds with 2 to 4 carbon atoms were summed. The extent of conversion of CO in the feed syngas to C_2 to C_4 compounds in the cooled reactor effluent gas was calculated and is shown in Figure 12. Conversion of CO to organic liquids was determined by difference, i.e. all of the converted CO which was not accounted for as CO_2, CH_4, or C_2-C_4 was assumed to be converted to organic liquids. This material was either removed from the reactor during the intermittent draining of the V-560 wax trap, the weekly draining of the 130°C trap (V-570), daily draining of the water cooled, near ambient temperature trap, or retained in the reactor and removed at the completion of the experiment. Figure 13 shows the fractional conversion of CO introduced to the reactor to liquid compounds. A two phase mixture was obtained when the water cooled trap (V-580) was drained before starting syngas flow each operating day. This mixture was composed of water produced by the reaction, and light organics that either volatilized from the organic products of reaction or from the wax reaction medium added to the reactor with the initial catalyst charge. Organics that would volatilize at ambient temperature would have been stripped from this mixture and accounted for in the chromatographic analysis of the reactor effluent gas. The production

rate of this mixture is shown in Figure 14. The mass of material collected during the weekly draining of trap V-570 was negligible in comparison to the mass drained from trap V-580. At the conclusion of the experiment, approximately 300 g of product wax plus catalyst was removed from the reactor. This material was solid at room temperature. This wax probably included most of the initial charge of 150 g of ASTM D-127 wax initially charged to the reactor as a reaction medium as well as the 10 g charge of iron-based catalyst. The product was black. The composition of the product wax is shown in Figure 15. The composition of the ASTM D-127 wax is also shown in Figure 15, for comparison purpose.

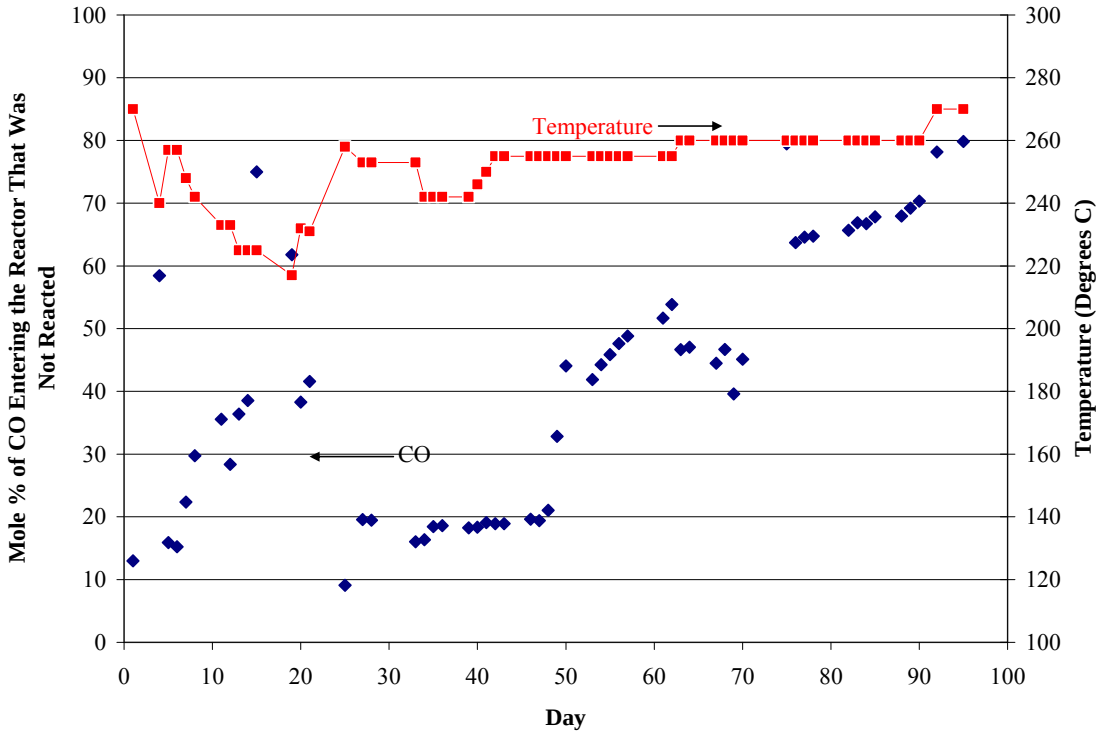

Figure 9: Unconverted Carbon Monoxide Present in Reactor Effluent, as a Percentage of Influent.

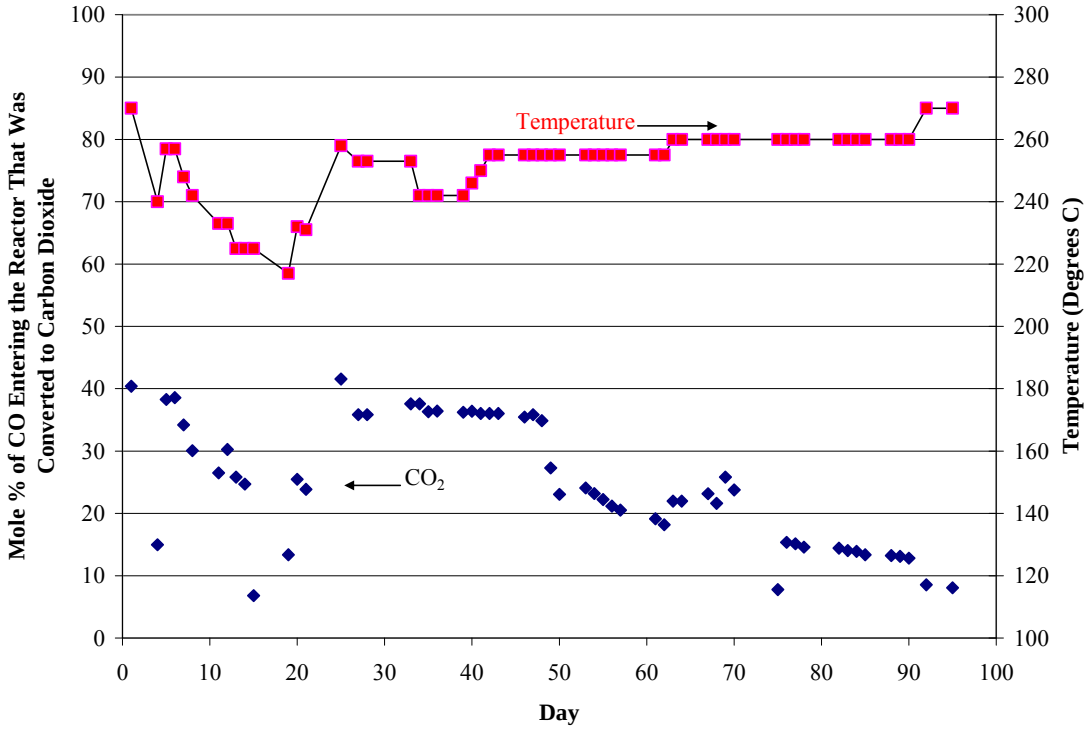

Figure 10: Conversion of CO to CO_2 in the CSTR with 10-g of activated iron-based catalyst.

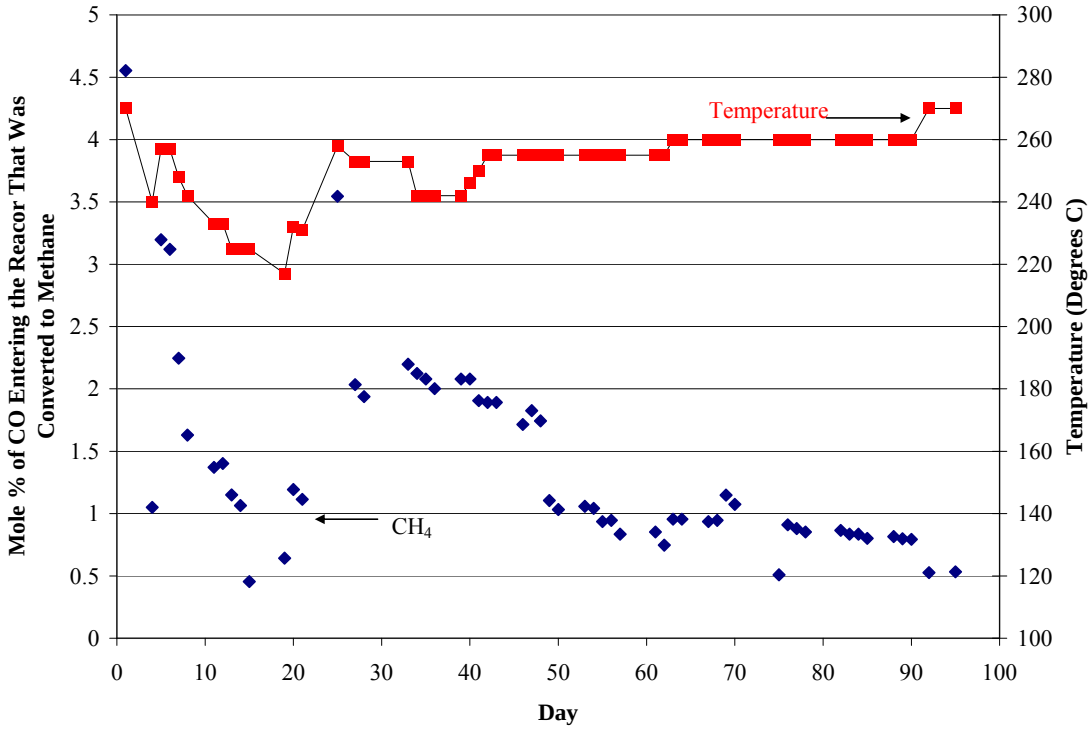

Figure 11: Conversion of CO to CH_4 in the CSTR with 10-g of activated iron-based catalyst.

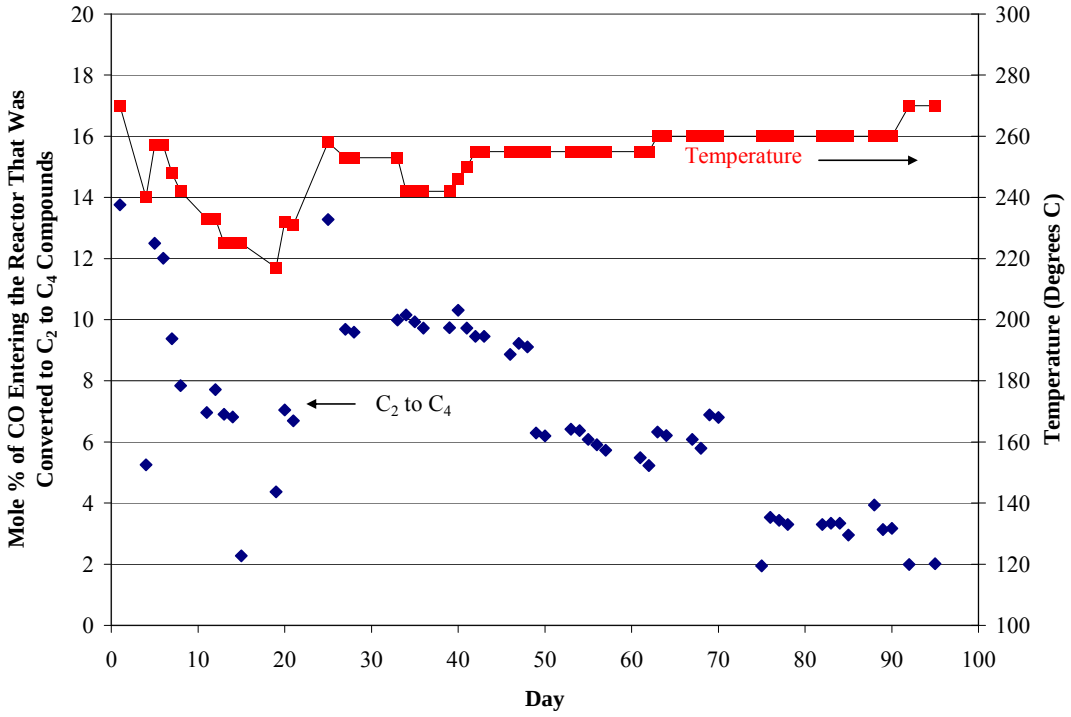

Figure 12: Estimated conversion of CO to C_2 to C_4 compounds in the CSTR with 10-g of activated iron-based catalyst.

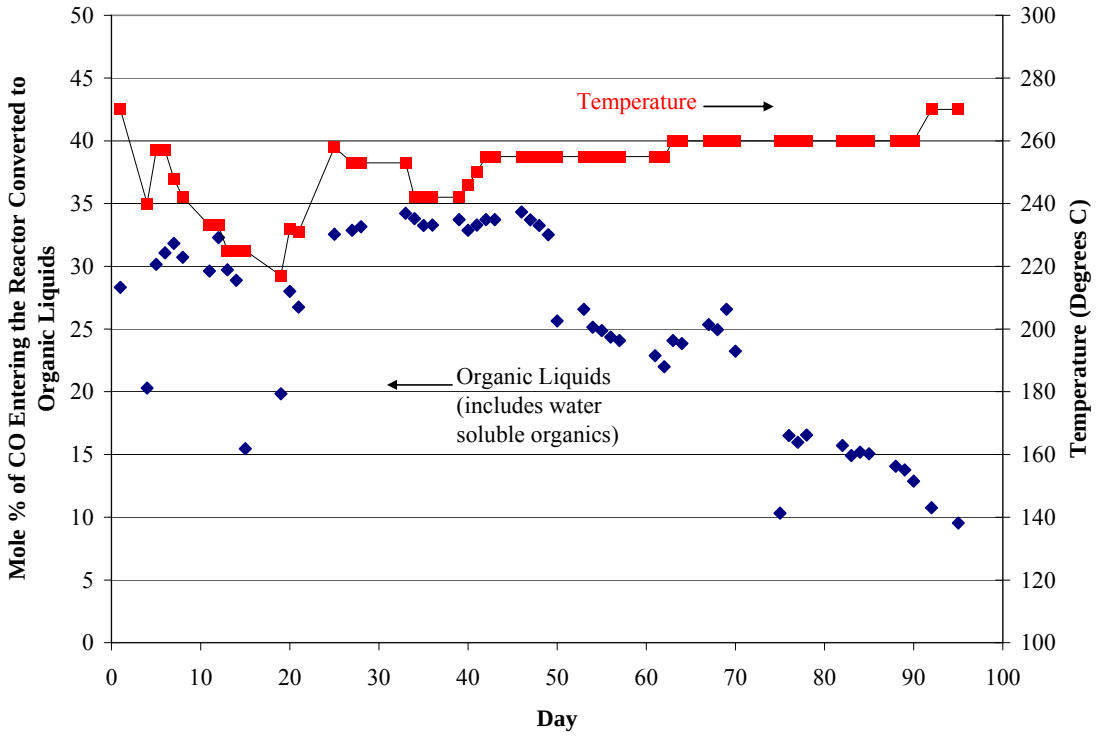

Figure 13: Estimated conversion of CO to organic liquids in the CSTR with 10-g of activated iron-based catalyst.

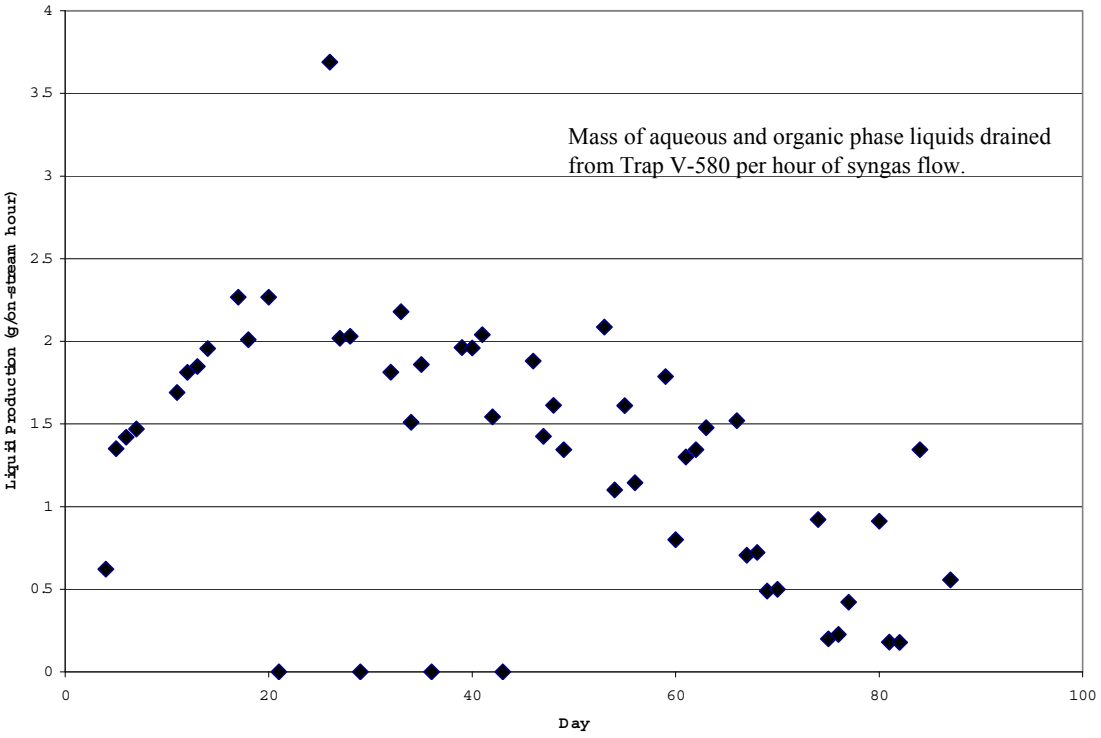

Figure 14: Liquid collected from daily draining of water-cooled trap V-580 (total of aqueous and organic phases.

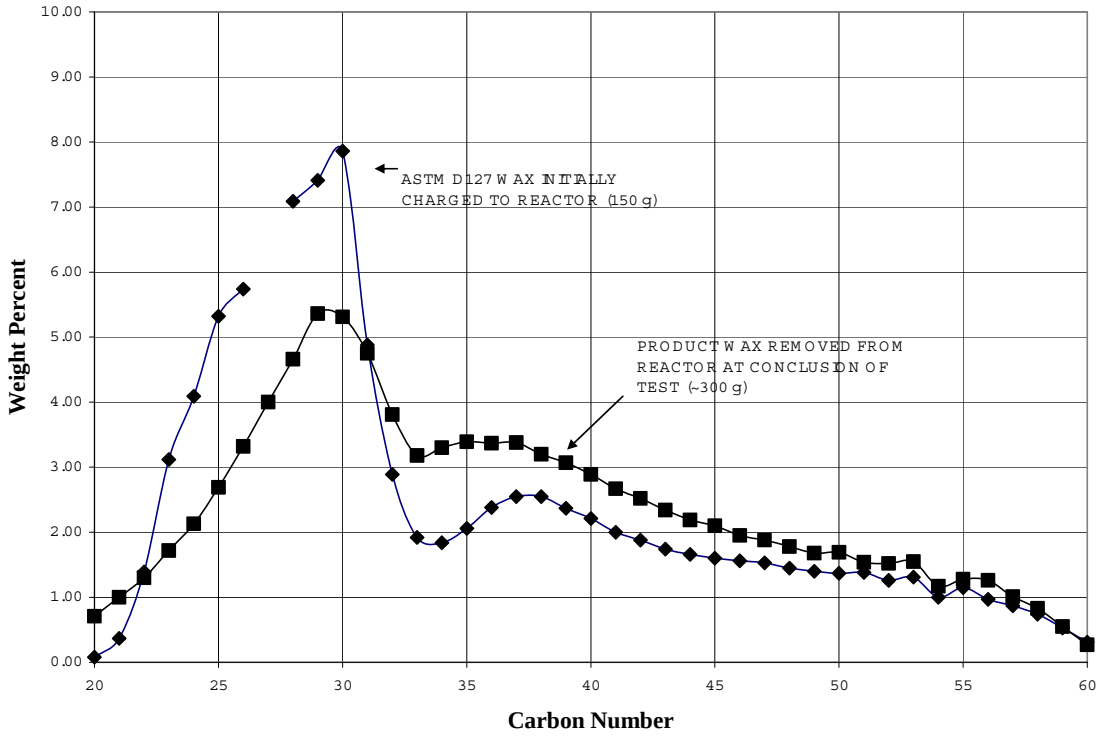

Figure 15: Composition of initial reactor charge and wax product removed from CSTR at conclusion of experiment

Effect of Temperature

In order to identify an appropriate temperature for the FT reactions using catalyst RTI-6, a series of tests were conducted to determine the effect of temperature on total conversion of CO, conversion of CO to CH4 and hydrocarbon yield, during the first 20 days of the preliminary extended time testing of RTI-6. Results of this study are summarized in Figure 16. According to Figure 16, as the temperature was increased from 217°C to 270°C, total CO conversion increased from about 38% to 88%, this led to an increase in yield of C_{2+} hydrocarbons from 155 to 275 mg of C/g-cat./h while the fraction of CO converted to CH_4 more than doubled. In the same temperature range, yields of C_{5+} hydrocarbons peaked at a temperature of 233°C and yields of CO_2 increased from 80 to 255 mg of C/g-cat./h. In the low temperature region, from 217 to 233 °C, selectivity towards CH_4 didn't change very significantly whereas the C_{2+} hydrocarbons yield increased from 155 to 250 mg/g.-cat./h which comprised of increase in C_{5+} hydrocarbons yields from 120 to 200 mg/g.-cat./h. At temperatures over 233 °C, with increasing CO conversion yields of C_{5+} hydrocarbons decreased with yields of C_{2+} hydrocarbons increasing only marginally from 250 to 275 mg/g.-cat./h. On the other hand, CH_4 selectivity more than doubled from 2 to 5 moles of CH_4 being produced for every 100 moles of CO reacted. A major portion of the CO conversion increase beyond 235°C is due to the water gas shift (WGS) reaction as seen from the increased CO_2 yield, which is undesirable.

These results show that the optimum operating temperature for this particular Fe catalyst under selected conditions is about 235°C where the yield of desired C_{5+} fraction is the maximum and the observed CO conversion is 70%. In a commercial embodiment, the unconverted CO could be recycled to the reactor to produce more desirable hydrocarbons.

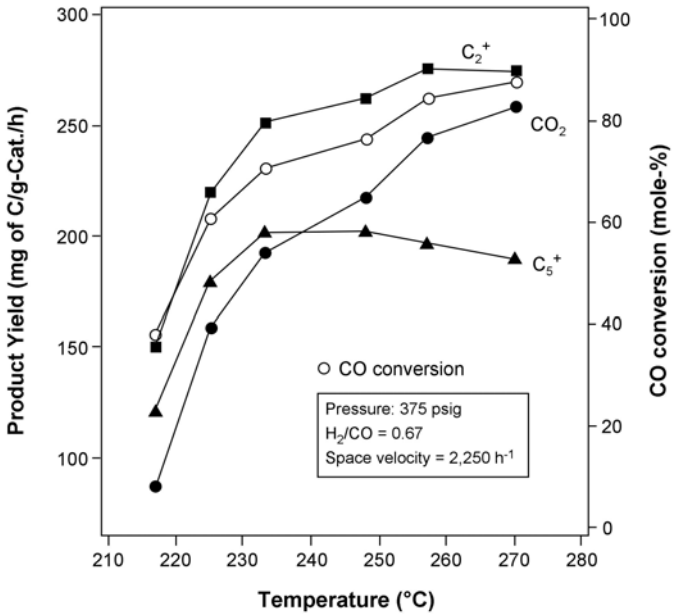

Figure 16: CO Conversion and Product Yield in a CSTR Using Catalyst RTI-6

Following the temperature ramp study, steady state operation was conducted in a temperature range of 250-260 °C. Catalyst activity was maintained throughout the duration of the 300 hours of operation, catalyst was able to maintain its activity. This is demonstrated by the fairly stable CO conversion and product yields as plotted in Figure 9 through Figure 14. Following 300 hours of operation (48 days), gradual catalyst deactivation was observed. This was attributed primarily to exposure of the catalyst to inert gas during overnight operation. Also, some deactivation was believed to be caused due to running at high conversion conditions for long periods of time. Steam formed from the reaction could re-oxidize the catalyst under these conditions.

Extended time testing of RTI-6

In order to avoid catalyst exposure to changing environment during interrupted operation, various modifications were made to the reactor system to be able to safely operate it unattended. Following these modifications, a CSTR test of the RTI-6 catalyst was performed from September 27, 2006 to October 19, 2006. The total time-on-stream for this experiment was slightly more than 500 hours. This test was initiated with 10-g catalyst and 150-g. Oronite Synthoil. Following a period of catalyst activation, the synthesis reaction was started. The nominal conditions for the reaction were 250-260°C (after a brief period of higher temperatures at the start of the test) at a total pressure of 375 psig. This run was planned at 240°C to understand the effect of lower temperature. The reactant gas was supplied from a premixed cylinder containing a 90%/10% mixture of CO and Ar and a cylinder of 100% H_2. The CO/Ar flow rate was 0.225 SLPM and the H_2 flow rate was 0.140 SLPM. The inlet H_2/CO mol ratio was about 0.7 which is typical of biomass-gasification syngas. After 330 hours of continuous operation, a power failure caused a period of 4 to 6 hours in which the temperature dropped, the agitator stopped and flows were disrupted. Conditions were restored and the test was resumed. About 48 hours before the end of the test, the agitator was stopped and synthesis gas flow was temporarily switched to N_2 to drain the product wax from the reactor at this time through a fritted dip tube. Syngas flow and agitation was then resumed. The temperature of the external reactor furnace was accordingly adjusted.

The reactor temperatures during the first two days of the test are shown in Figure 17. Occasional minor adjustments to the furnace set point were made to compensate for declining reaction rates as the test progressed.

Overall CO conversion for the entire 500 hour time-on-stream period is shown in Figure 18. At the reaction temperature of 240^{o}C, consistent conversion of about 40% was observed in the period between about 150 and 420 hours of on-stream time. The reaction rate was apparently unaffected by the brief period of interrupted agitation and syngas flow. The conversion fell rapidly after 420 hours because of catalyst over-carburization. As is apparent from our previous experience with this catalyst, this could be avoided by simply running at about 20^{o}C higher temperature or with a higher inlet H_2/CO mol ratio syngas.

The product yield as a function of on-stream time is shown in Figure 19. These data for CH_4, CO_2 and C_1 through C_4 compounds were determined by hourly chromatographic analyses of the non-condensable fraction of the reactor exit gas. The C_{5+} yield was determined by difference (based on the input of CO). During the "steady-state"

period of operation the production of C_{5+} compounds was approximately 0.14 g carbon/(g catalyst-hr) in contrast to a CO_2 yield of approximately 0.09 g carbon/(g catalyst-hr).

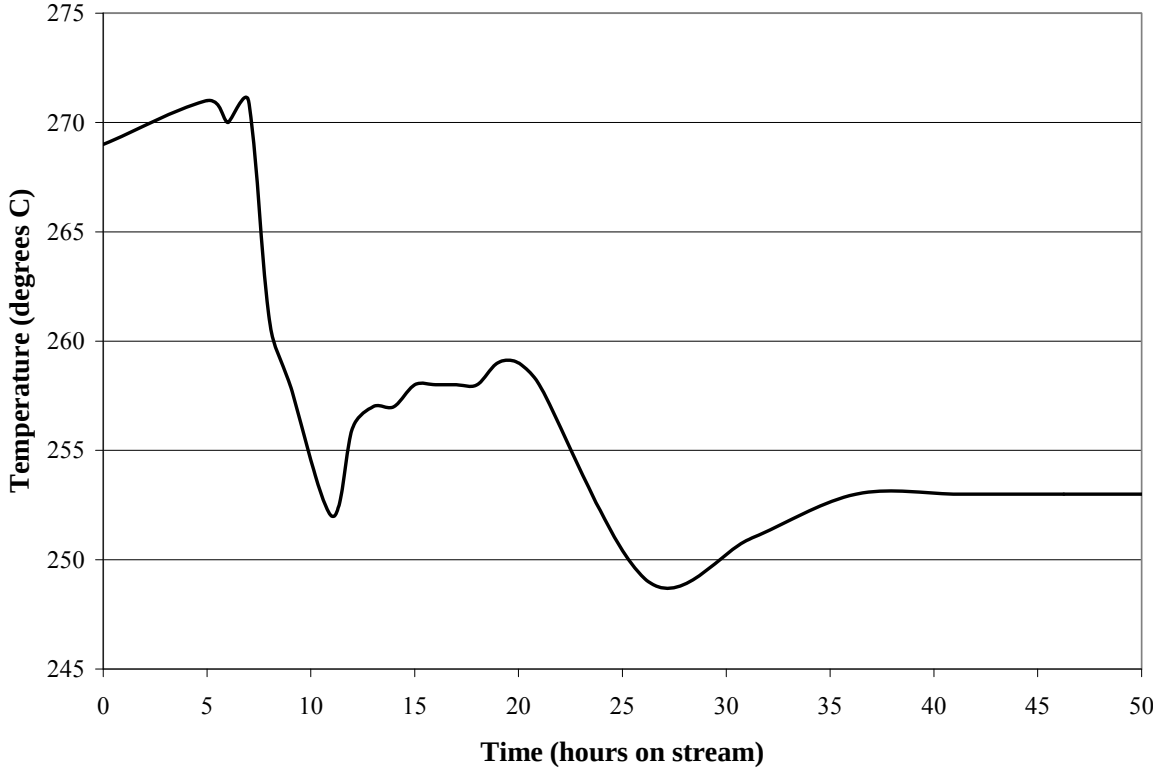

Figure 17: Reactor temperature during the first two days of testing

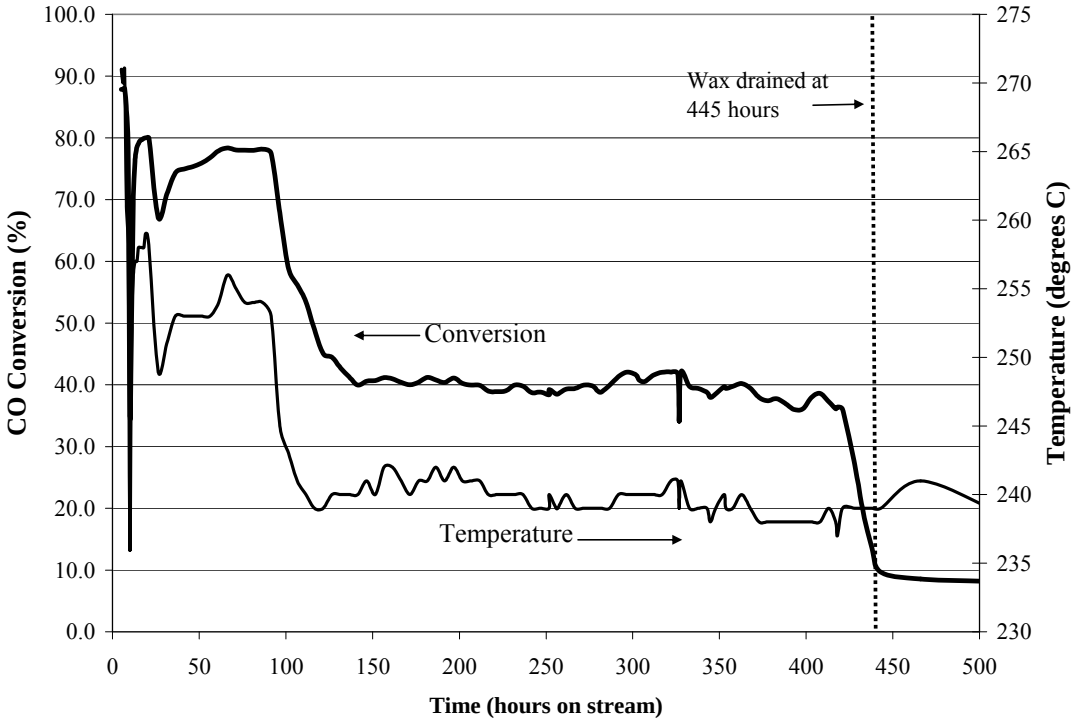

Figure 18: CO conversion and temperature for 500-hour continuous test

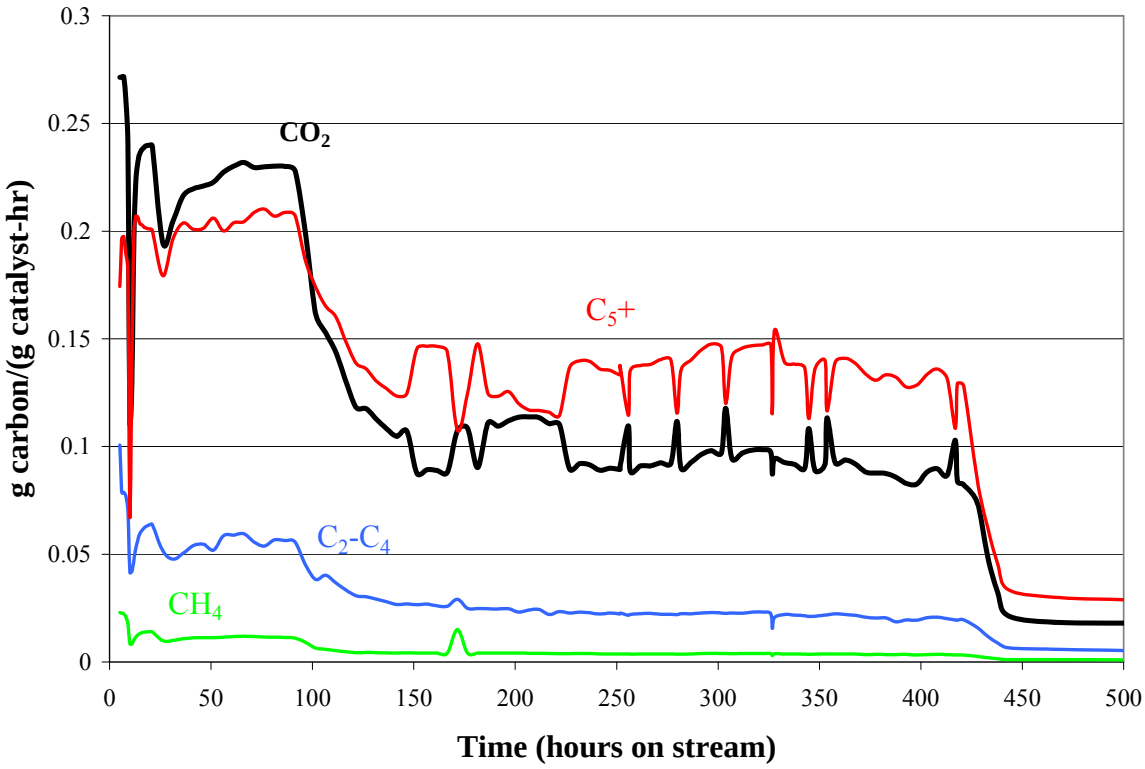

Figure 19: Product yield and CO_2 production during 500-hour continuous test

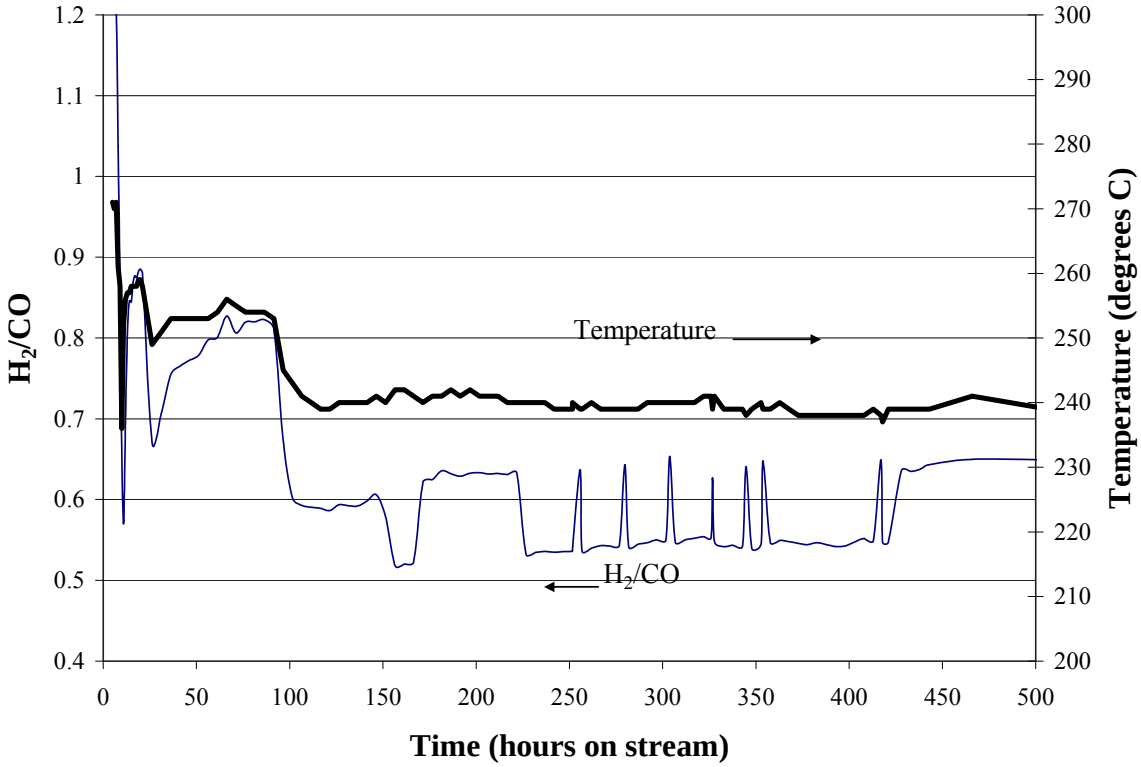

Figure 20: Ratio of H_2 to CO in gas at exit of reactor during 500-hour test

The mol ratio of H_2 to CO in the reactor exit gas is shown in Figure 20. During the "steady state" period of the test H_2/CO ratio was roughly 0.6. The run was purposely performed at these highly carburizing conditions to determine how rugged the catalyst was at these conditions. The ratio is influenced by both the consumption of reactants and the water gas shift activity of the catalyst. By running at somewhat higher temperature, a greater shift activity could be maintained thereby increasing the H_2/CO mol ratio.

The reactor exit gas passes through two liquid product and steam knockout traps before entering the GC analysis loop and exhaust vent. The first trap was maintained at approximately 120-150°C with an external heating tape and the second trap was cooled to approximately 20°C with a water cooled jacket. These traps were drained as necessary and the liquid samples from the traps were combined. The resulting composite generally composed of an aqueous phase and an organic phase were weighed. Liquid production data for the test are shown in Figure 21.

The contents of the liquid knockout were divided into three samples corresponding to the initial high reaction rate stage (9/29/2006-10/2/2006), the steady state stage (10/3/2006-10/17/2006) and the end of the test (10/18/2006-10/20/2006). The organic phase of each of these samples was analyzed chromatographically. Distribution of organics in these samples, summed by carbon number, is shown in Figure 22. The aqueous phase of the composite sample from the steady state stage of the test was analyzed by gas chromatography/mass spectroscopy (GC/MS). A total ion chromatogram of this sample is shown in Figure 23. GC/MS analysis has resulted in identification of 33 distinct oxygenated species in this sample with ethanol as one of the major species.

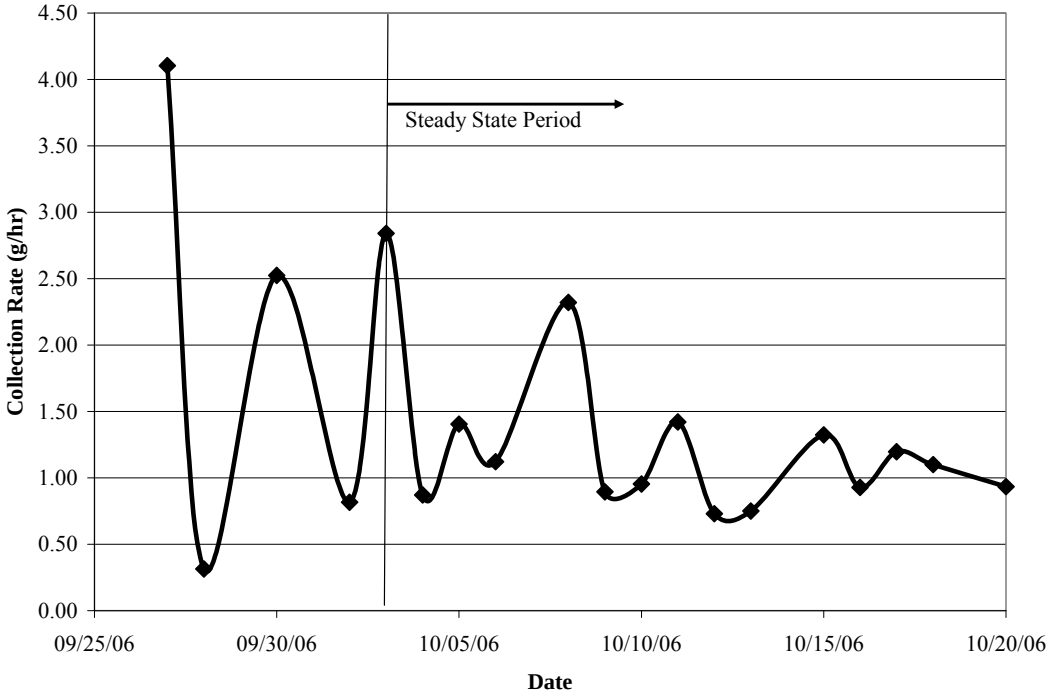

Figure 21: Combined aqueous and organic phase liquid production from liquid knockout traps during 500-hour test

After 445 hours on stream, the wax product was drained from the reactor through a fritted dip tube. At the conclusion of the test, the reactor was opened and an additional 330 g of product wax and catalyst was removed. Figure 24 shows the carbon number distribution of the drained wax sample, as well as the average of two replicate analyses of the wax product removed from the reactor at the conclusion of the test. The carbon number distribution of the initial reactor charge (Oronite Synfluid) is also shown in this figure. Compounds shorter than C_9 are not present in these analyses. Presumably these compounds were either recovered in the knockout traps or discharged as gases to the product gas exhaust. Compounds longer than C_{60} may have been present but were not determined by the chromatographic method that was used.

A chromatogram of one product wax sample (final reactor contents) is superimposed on a chromatogram from the initial reactor charge (Oronite Synfluid) in Figure 25. By observing the peaks from this chromatogram shows that the catalyst has a very high alfa number (~0.95) under these test conditions, as evident from the peaks from C_{18}-C_{23}.

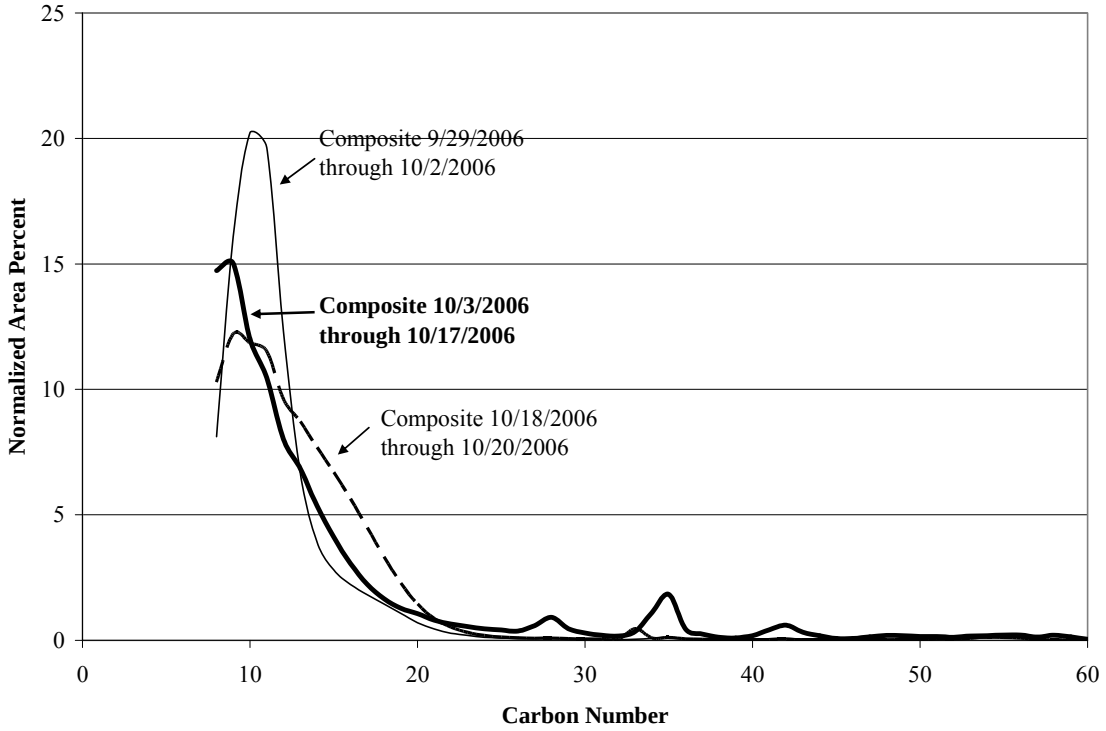

Figure 22: Carbon number of organic phase composites from traps V-570 and V-580 for 500-hour test

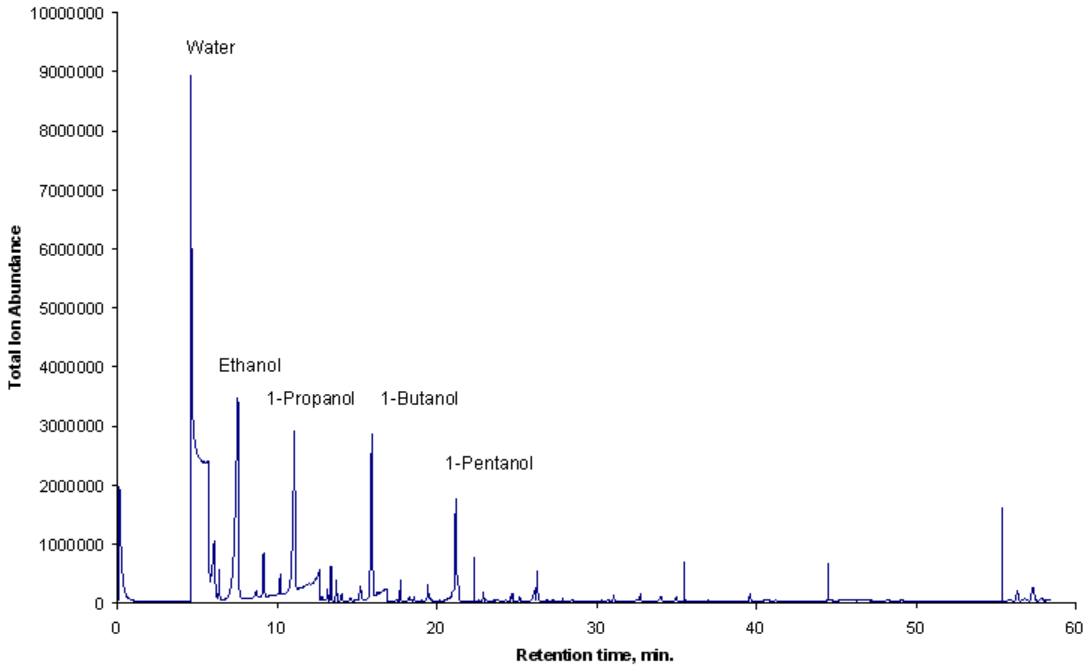

Figure 23: Total ion chromatogram of aqueous phase of composite from traps V-570 and V-580 during steady-state period of 500-hour test

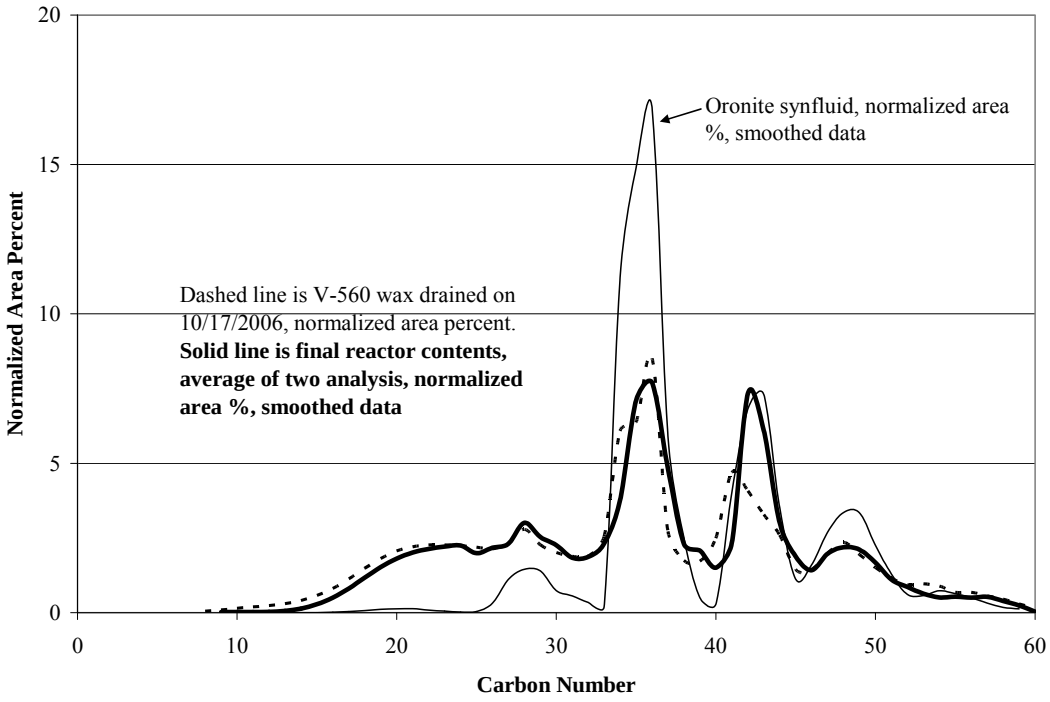

Figure 24: Carbon number distribution of product wax and initial reactor charge from 500-hour test

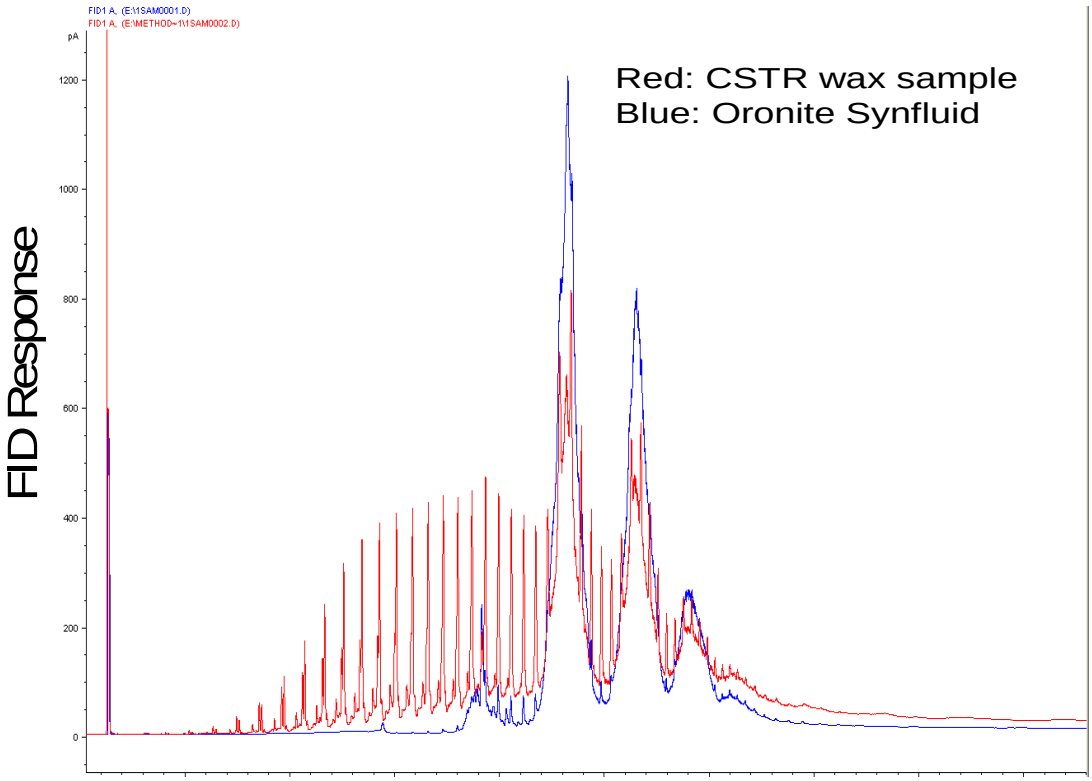

Figure 25: Chromatograms of initial charge and product wax.

Task 3 – Development of a Selective Catalytic Process for the Synthesis of Alcohols

W.R. Grace was secured as a cost-chare partner for this task. Based on the contractual agreement with them, RTI was to test catalyst samples provided by Grace. Chemical and physical properties of these catalysts were not known and were considered proprietary information of Grace. Throughout the project duration, W.R. Grace provided 23 catalyst samples for testing at RTI in the dual microreactor systems with bottled syngas. Initially, a test plan was developed that included pretreatment protocols for sulfiding the catalysts and specified reactor conditions. Based on the observed results, selected catalysts were tested at different operating parameters such as temperature and space velocity and under slightly varying protocols. A summary of all the tests performed, along with the results obtained, is provided in Table 1.

Begin Proprietary and Confidential Information

The results showed little to moderate productivity using catalysts from the 18895 series for mixed alcohol synthesis from bottled syngas with a H_2/CO molar ratio between 1.0-1.2 in a temperature range from 300-350°C. Reactor pressure was maintained at 900psi. Based on the results from these screening studies additional catalysts were supplied by Grace.

The next set of catalysts was from the 44-1 series. The first four catalysts of this series presented higher CO conversion in the temperature range of 325-350°C. Liquid products were obtained using these catalysts with catalyst 44-1-4 providing the best EtOH selectivity of 6.4%. From the same series, catalysts 44-1-5 and 44-1-6 presented slightly lower CO conversion compared to earlier catalysts but a significant improvement in selectivities of higher alcohols was observed. Catalyst 44-1-5 was tested at three different temperatures, two different space velocities and also in presence of H_2S in the feed. Increasing temperature from 300 to 350 °C increased CO conversion from 14 to 37%. Selectivity towards CO_2 and CH_4 remained unchanged with temperature whereas increasing temperature increased selectivity towards higher carbon number alcohols. Presence of H_2S in the feed didn't change the performance of the catalyst. Improvement in higher alcohol selectivity was further observed using catalyst 44-1-6 at the expense of decreased selectivity of C_{2+} hydrocarbons.

Similar set of tests were conducted with catalysts from 76 series. Again, presence of H_2S in the feed didn't change the performance of catalyst. CO conversion was higher (36%) at lower space velocity of ~485 hr^{-1}. At the same condition, selectivity of $C_{4+}OH$ was higher (22%). At a higher space velocity of ~985 hr^{-1}, CO conversion decreased to 28% whereas the catalyst selectively produced other oxygenate compounds. Similarly higher selectivity of 50% towards higher alcohols was observed using catalyst 76-11C. Rest other catalysts in this series were more selective towards higher hydrocarbons and were not effective in producing higher alcohols.

Table 1: Operating conditions and results of higher alcohol synthesis reactions using WR Grace catalysts

Manufacturing Number	18895-Sample #									190Sample #													190Sample #												
Sample	182-1	182-1	182-1	182-4	182-6	182-7	182-5	182-2	182-3	44-1-1	44-1-2 T1	44-1-2 T2	44-1-2 T3	44-1-3	44-1-4	44-1-5 T1	44-1-5 T2	44-1-5 T3	44-1-5 T4	44-1-5 T5	44-1-6 T1	44-1-6 T2	76-11F T1	76-11F T2	76-11F T3	76-11F T4	76-11F T5	76-12C T1	76-12A T1	76-11D T1	76-11A T1	76-11C T1	76-12B T1	76-11E T1	76-11B T1
Final Sulfiding Temp (°C)	246	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316	316
Space Velocity (hr^{-1})	8000	8000	8000	2000	2000	1000	1000	1000	1000	987	996	984	984	996	1001	1001	1014	1014	1145	1108	964	957	486	985	491	987	492	999	998	1005	1002	1000	1003	1000	1000
Catalyst Sample Size (g)	0.57	0.56	0.56	2.7	2.74	4.77	4.41	4.95	5.54	5.96	5.95	5.98	5.98	6.59	6.92	7.34	7.24	7.24	7.14	7.35	9.35	9.37	10	10	10.1	10.1	10.1	9.98	8.5	8.51	8.5	9.98	8.58	9.52	9..5
H_2/CO Ratio	1	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Operating Temp (°C)	300	300	350	350	350	325	325	325	325	325	325	300	350	325	325	325	300	350	325	325	325	325	325	325	325	325	325	325	325	325	325	325	325	325	325
Pressure (psi)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
H_2S in Syngas (ppm)	100	100	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0	100	0	0	100	100	100	100	100	100	100	100	100	100	100
CO Conversion (%)	~5-10	~4-6	~6-12	35	33	30	11	30	26	55	38	17	55	38	34	27	14	37	26	28	21	22	36	28	37	26	34	19	33	73	78	24	24	42	57
Wt Units CO converted per Wt Unit of catalyst per hr (g/g_{cat}*hr)	0.54	0.30	0.66	0.50	0.53	0.29	0.11	0.26	0.21	0.41	0.28	0.12	0.41	0.26	0.22	0.16	0.08	0.23	0.17	0.18	0.10	0.11	0.11	0.16	0.11	0.16	0.10	0.12	0.27	0.50	0.54	0.14	0.17	0.26	0.36
CO_2 Production (%) (mol CO_2/mol CO Conv)	14	26	36	41	45	44	40	45	45	47	45	43	46	46	43	41	37	43	40	40	37	38	41	38	40	38	40	36	44	46	46	39	43	43	44
	Selectivity Based on Total Carbon Moles Gas Phase Components (CO_2 Free) - Contains Hydrocarbons from Liquid Phase									Selectivity Based on Total Carbon Moles Gas Phase Components (CO_2 Free) - Contains Hydrocarbons from Liquid Phase													Selectivity Based on Total Carbon Moles Gas Phase Components (CO_2 Free) - Contains Hydrocarbons from Liquid Phase												
CH_4 Carbon Mol Selectivity (%)	20	21	33	40	38	33	32	25	30	37	31	27	37	28	40	38	35	36	36	38	33	31	27	17	30	22	23	36	31	39	46	32	32	25	27
C_{2+} Carbon Mol Selectivity (%)	80	79	67	61	62	66	68	74	70	63	63	68	59	64	35	15	14	14	12	13	5	5	15	12	16	13	13	6	64	58	53	16	56	50	48
	Selectivity Based on Total Carbon Moles Liquid Phase Components (CO_2 Free)									Selectivity Based on Total Carbon Moles Liquid Phase Components (CO2 Free)													Selectivity Based on Total Carbon Moles Liquid Phase Components (CO2 Free)												
MeOH Carbon Mol Selectivity (%)	—	—	—	0.05	—	0.33	—	0.40	NA	0.0	2.3	0.5	1.6	2.9	1.4	2.9	4.1	1.7	3.8	2.9	5.1	4.8	2.8	5.9	2.9	5.5	3.9	7.0	1.1	1.2	1.3	4.4	2.2	4.1	4.2
EtOH Carbon Mol Selectivity (%)	—	—	—	0.09	—	0.53	—	0.80	0.53	0.2	1.9	1.5	1.7	3.1	6.4	14.8	21.0	6.7	19.0	16.0	21.0	20.0	12	12	12	12	10	14.9	0.8	0.7	0.3	15.0	4.7	6.9	4.8
PrOH Carbon Mol Selectivity (%)	—	—	—	0.01	—	0.11	—	0.28	0.17	0.0	0.6	0.9	0.6	1.9	7.0	12.6	14.0	9.6	15.0	13.0	18.0	18.0	14	12	13	12	11	17.0	1.0	0.5	0.04	13.0	3.5	6.5	5.5
C4+OH Carbon Mol Selectivity (%)	—	—	—	0.00	—	0.00	—	0.04	0.03	0.0	0.1	0.6	0.2	0.5	7.4	12.6	9.8	20.0	11.7	13.0	13.0	13.9	22	14	20	15	13	16.0	0.9	0.4	0.03	15.7	2.2	6.8	8.5
Other Oxygenates Carbon Mol Selectivity (%)	—	—	—	0.00	—	0.00	—	0.00	0.00	0.0	0.0	4.0	0.02	0.0	3.4	4.0	3.6	13.0	5.1	5.7	6.3	7.8	7	25	4.4	21	25	4.5	0.0	0.0	0.0	3.5	0.0	0.5	1.6
Selectivity Total	100	100	100	101	100	100	101	100	101	100	99	102	100	100	101	100	102	101	103	102	101	101	99	98	98	101	99	101	99	100	101	100	101	100	100

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Task 4. Modeling, Engineering Evaluation, and Commercial Assessment

Various syngas utilization opportunities were evaluated. Details of this review are provided in Appendix 1. Our evaluation showed that both diesel and mixed alcohols are attractive products from biomass. Both cobalt and iron catalysts could be used for diesel synthesis. Cobalt would require an additional water-gas shift step prior to the synthesis. Iron is preferred for biomass-derived syngas because it can handle a low H_2/CO mol ratio syngas, and is somewhat more tolerant to contaminants in the syngas. Our RTI-6 iron catalyst appears well suited for biomass syngas conversion to diesel. It needs to be run at about 260^{o}C, preferably in the 255-270^{o}C range.

A commercial catalyst for direct syngas conversion to ethanol with high alcohol selectivity is yet to be developed. Other routes such as methanol homologation and condensation should also be evaluated. It is difficult to avoid significant methane formation with currently proposed catalysts, such as Cu-Co and Rh-Fe that also give relatively high selectivity for ethanol. We believe that the use of noble metal (Rh-based) catalysts should be avoided for mixed alcohol synthesis due to cost reasons. The most viable catalysts to date appear to be MoS_2, Cu-Co and Cu-Zn, and should be evaluated for alcohol and ethanol synthesis routes other than simply direct synthesis.

Conclusions

The goals for this project were met by developing bench-scale reactor systems to evaluate the performance of catalysts to convert syngas to liquid fuels, specifically FT diesel and mixed alcohols. Microactivity tests reactors were designed and fabricated to test the activity and selectivity of selected FT and mixed alcohol catalysts. Long-term testing (> 500 hours time on stream) of RTI's proprietary Fe-based FT catalysts was completed in a laboratory-scale continuously stirred tank reactor. Catalyst activity over time was measured to evaluate long term catalyst deactivation.

Mixed alcohol catalyst development and testing was done in collaboration with WR Grace, our industrial catalyst partner in the project. WR Grace provided 23 different catalyst formulations that were tested in the microactivity test systems at RTI. Progress was made in determining the more productive formulations. CO conversion efficiency were in the range of 20-50% with modest C_2+ productivity; however, the CO_2 and CH_4 yields were higher than desired. Additional development is required to reduce the CO_2 and CH4 yields and increase the higher alcohol yields.

A through review of recent literature on syngas to ethanol was prepared. More then 220 publications and patents were reviewed. The review looked at various routes and chemistries of converting syngas to ethanol. Thermodynamic calculations were also presented to understand the limits on various reactions as a function of process parameters. Past research efforts in developing catalysts and reactor designs were extensively discussed to finally summarize the R&D needs in commercializing syngas conversion to ethanol.

Based on this review of the literature, no systematic study has been done in the past to optimize mixed alcohol synthesis from syngas and to efficiently integrate the synthesis and separation steps into an overall biomass gasification plant. HAS commercial success has been limited by low yield and selectivity, although a few pilot plants, ranging from 2 to 400 ton/day, have been built and operated. Syngas can be converted to ethanol directly using rhodium-iron-based catalysts; however, selectivity for this conversion is low and the rhodium catalyst is very expensive. Mixed alcohol synthesis (C1 to C5 alcohols) is a more desirable route particularly when coupled with methanol homologation to increase the ethanol yield. Mixed alcohol synthesis and methanol homologation catalysts are similar and consist of a combination of alkali-promoted base metals (e.g. Cu, Zn, Co, Mo) on oxide supports. Catalysts of particular interest for further improvement include Cu-Co, unsulfided Co-Mo, and unpromoted and cobalt-promoted MoS2. Current total alcohol yields from these catalysts are in the 0.1 to 0.6 g/g catalyst/h range as compared to the bench-mark 1.3 to 1.5 g/g catalyst/h methanol yield in the commercially practiced methanol synthesis process. Also, hydrocarbons and CO_2 are produced thereby reducing total alcohol and ethanol selectivities.

The main challenge is to produce an ethanol-rich product from biomass-derived syngas that will be cost competitive with corn-based or petroleum-based ethanol. A systematic experimental process development and process integration study is still needed to optimize the syngas conversion process and to efficiently integrate the synthesis and separation steps into an overall biomass gasification plant. The bench-scale catalyst studies in this project have identified future directions for catalyst development. Although activity and selectivity of the present catalysts are presumably the main technical barriers, system studies must go hand-in-hand with catalyst/reactor improvement studies to develop realistic yield and selectivity targets for ethanol synthesis from biomass-derived syngas.

References

1. Phillips, S.D., *Technoeconomic analysis of a lignocellulosic biomass indirect gasification process to make ethanol via mixed alcohols synthesis.* Industrial & Engineering Chemistry Research, 2007. **46**(26): p. 8887-8897.
2. Herman, R.G., *Advances in catalytic synthesis and utilization of higher alcohols.* Catalysis Today, 2000. **55**(3): p. 233-245.
3. Wender, I., *Reactions of synthesis gas.* Fuel Processing Technology, 1996. **48**(3): p. 189-297.
4. Fierro, J.L.G., *Catalysis in C1 chemistry: future and prospect.* Catalysis Letters, 1993. **22**(1-2): p. 67-91.
5. Courty, P., et al., *Production of methanol-higher alcohol mixtures from natural gas via syngas chemistry.* Revue de l'Institut Francais du Petrole, 1990. **45**(4): p. 561-78.

Appendix 1 – Energy and Fuels Publication: A Review of Recent Literature to Search for and Efficient Catalytic Process for the Conversion of Syngas to Ethanol

A vast amount of literature exists that describes the scientific and commercial advancements that have been made in syngas chemistry over the years. The purpose of this review was to summarize the catalysts and processes developed for mixed alcohol synthesis to attempt to identify commercially promising catalyst materials and processes and uncover gaps that require additional R&D to help advance a commercially-viable thermochemical biomass conversion process to produce ethanol. The timeliness and usefulness of this publication is evident by the number of times it has been cited since it was published. The American Chemical Society journal Energy&Fuels has recently announced that this publication was one of the top 20 most cited publications in 2008.

Reviews

A Review of Recent Literature to Search for an Efficient Catalytic Process for the Conversion of Syngas to Ethanol

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Received July 16, 2007. Revised Manuscript Received September 10, 2007

Alternatives to petroleum-derived fuels and chemicals are being sought in an effort to improve air quality and increase energy security through development of novel technologies for the production of synthetic fuels and chemicals using renewable energy sources such as biomass. In this context, ethanol is being considered as a potential alternative synthetic fuel to be used in automobiles or as a potential source of hydrogen for fuel cells as it can be produced from biomass. Renewable ethanol can also serve as a feedstock for the synthesis of a variety of industrial chemicals and polymers. Currently, ethanol is produced primarily by fermentation of biomass-derived sugars, especially those containing six carbons, whereas 5-carbon sugars and lignin, which are also present in the biomass, remain unusable. Gasification of biomass to syngas ($CO + H_2$), followed by catalytic conversion of syngas, could produce ethanol in large quantities. However, the catalytic conversion of syngas to ethanol remains challenging, and no commercial process exists as of today although the research on this topic has been ongoing for the past 90 years. Both homogeneous and heterogeneous catalytic processes have been reported. The homogeneous catalytic processes are relatively more selective for ethanol. However, the need for expensive catalyst, high operating pressure, and the tedious workup procedures involved for catalyst separation and recycling make these processes unattractive for commercial applications. The heterogeneous catalytic processes for converting syngas to ethanol suffer from low yield and poor selectivity due to slow kinetics of the initial C–C bond formation and fast chain growth of the C_2 intermediate. Recently, there is a growing worldwide interest in the conversion of syngas to ethanol. Significant improvements in catalyst design and process development need to be achieved to make this conversion commercially attractive. This paper reviews and critically assesses various catalytic routes reported in the recent past for the conversion of syngas to higher alcohols, with an emphasis on ethanol. The chemistry and thermodynamics of the processes, the type of catalysts developed, reactors used, and the current status of the technology are reviewed and discussed.

1. Introduction

Increasing concerns about global climate change, depletion of fossil fuel resources, and rising crude oil prices have pushed the topic of energy to the center stage. The International Energy Administration estimates that the world marketed energy consumption will increase from 447 quadrillion Btu in 2004 to 702 quadrillion Btu in 2030 and that the majority of this energy will be produced from fossil fuels, especially from coal and oil.[1–3] Consequently, the world oil consumption is expected to grow from 80 million barrels per day in 2003 to 98 million barrels per day in 2015 and 118 million barrels per day in 2030. However, because oil is concentrated only in few regions of the globe and the oil reserve is declining, research in the development of synthetic fuels technology using alternative energy sources such as biomass has become increasingly important in recent years.[4,5]

Biomass includes various plant components, such as starch, cellulose, hemicellulose, and lignin. While starch and cellulose are biopolymers of glucose, a 6-carbon sugar (hexose), the hemicellulose is primarily pentosans or polymeric pentose, mostly xylose, and lignin is polymeric phenyl propane. Biomass can be converted into a wide range of liquid fuels, called "biofuels," such as bioethanol, biodiesel, liquid alkanes, and furfural and its derivatives for future transportation fuel needs.[6–15] Among them, bioethanol received considerable inter-

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(1) Energy Information Administration (EIA). *International Energy Outlook*; U.S. Department of Energy: Washington, DC, 2007; www.eia.gov/oiaf/ieo/index.html.

(2) International Energy Agency. Global Energy Outlook: Issues and Challenges. *10th International Energy Forum*, April 22–24, 2006.

(3) Song, C. *Catal. Today* **2006**, *115*, 2.

(4) Hahn-Hagerdal, B.; Galbe, M.; Gorwa-Grauslund, M. F.; Liden, G.; Zacchi, G. *Trends Biotechnol.* **2006**, *24*, 549.

(5) Petrus, L.; Noordermeer, M. A. *Green Chem.* **2006**, *8*, 861.

(6) Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. *Science* **2005**, *308*, 1446.

(7) Koonin, S. E. *Science* **2006**, *311*, 435.

(8) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederic, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R. *Science* **2006**, *311*, 484.

(9) Demirbas, A. *Prog. Energy Combust. Sci.* **2007**, *33*, 1.

(10) Pimentel, D.; Patzek, T. W. *Nat. Resour. Res.* **2005**, *14*, 65.

10.1021/ef700411x CCC: $40.75
Published on Web 01/31/2008

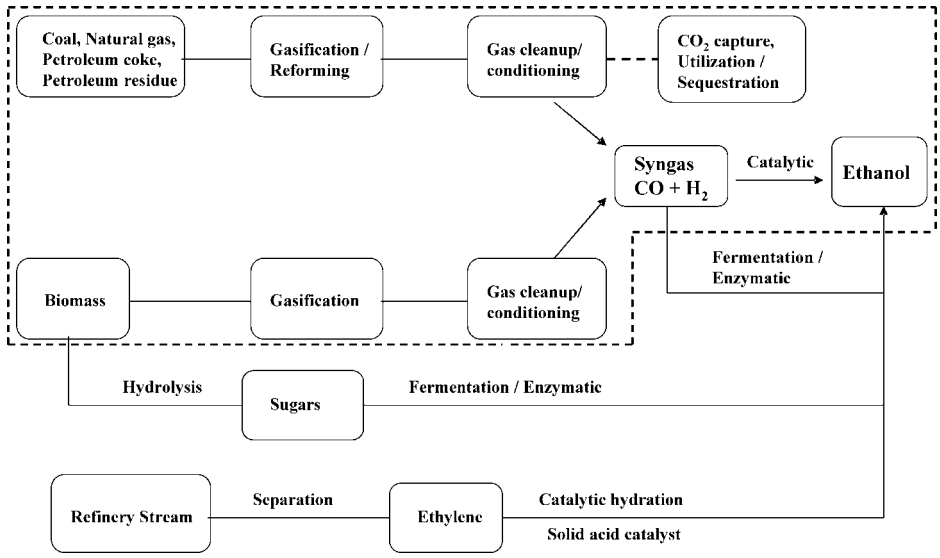

Figure 1. Synthesis of ethanol from various carbon-containing feedstocks. The focus of this review is shown in dotted lines.

est in recent years to use in automobiles, either as an additive or as a potential substitute for gasoline. The use of ethanol as a gasoline additive is already in practice in the United States (U.S.) and other countries. Studies have shown that the use of ethanol as a fuel in automobiles offers the same chemical energy as that of gasoline but with less emission of greenhouse gases (GHGs) and other environmental pollutants, especially when it is produced from cellulose rather than from cornstarch[16] although the energy, economic, and environmental benefits of bioethanol as a gasoline substitute are still under debate.[17–19]

In addition to its potential application as a transportation fuel, bioethanol has been considered as a feedstock for the synthesis of variety of chemicals, fuels, and polymers.[20–22] Bioethanol is also being considered very recently as a potential source of renewable hydrogen in fuel cell applications.[23–25] Consequently, there is a growing worldwide interest in the production of ethanol from biomass and possibly from other readily available carbonaceous sources such as coal without CO_2 emission, and its use as a fuel for transportation, chemical feedstocks, and as an H_2 carrier in the future.[26,27]

Worldwide ethanol production in 2005 exceeded 12 billion gallons, with Brazil and the United States being the largest producers in the world, each contributing over 4.2 billion gallons. A major portion of the ethanol produced in the United States was used for blending with gasoline, but this mixture replaced only about 2% of all gasoline sold. The Energy Policy Act (EPACT) of 2005 requires U.S. fuel ethanol production to increase to 7.5 billion gallons by 2012.[16] This has prompted a significant increase in the research and development (R&D) effort dedicated to this challenge.

Currently, ethanol is produced by two major processes: (1) fermentation of sugars derived from corn or sugar cane and (2) hydration of petroleum-based ethylene, as shown schematically in Figure 1. Although the hydration of ethylene over a solid acid catalyst is used for the production of industrial-grade pure ethanol,[28] the fermentation of sugars is a biological process for producing beverage-grade alcohol containing about 14% ethanol. The ethylene hydration route is unattractive for large-scale production of ethanol because of rising crude oil prices and the dependence on imported oil. Although the fermentation route is commercially practiced for the production of most of the ethanol produced today, the production of fuel-grade ethanol is expensive and energy-inefficient because the process involves energy-intensive distillation steps.[29] Furthermore, the current fermentation process is not suitable for sugars derived from lignocellulose or woody biomass because they contain a significant portion of 5-carbon pentose sugars (in addition to 6-carbon hexose sugars), which are not completely metabolized into alcohol by the micro-organisms used in the fermentation process.[30,31] Because of this constraint, the current fermentation process is limited in its application only to selected biomass components for ethanol production. New fermentation processes that can convert both 5- and 6-carbon sugars into ethanol, as well as the fermentation of syngas (a mixture of CO and H_2) obtained from gasification of

(11) Wesseler, J. *Energy Policy* **2007**, *35*, 1414.
(12) Roman-Leshkov, Y.; Barrett, C.; Liu, Z. Y.; Dumesic, J. *Nature* **2007**, *447*, 982.
(13) Schmidt, L. D.; Dauenhauer, P. J. *Nature* **2007**, *447*, 914.
(14) Chheda, J. N.; Roman-Leshkov, Y.; Dumesic, J. *Green Chem.* **2007**, *9*, 342.
(15) Zho, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. *Science* **2007**, *316*, 1597.
(16) Farrell, A. E.; Plevin, R. J.; Turner, B. T.; Jones, A. D.; O'Hare, M.; Kammen, D. M. *Science* **2006**, *311*, 506.
(17) Reisch, M. *Chem. Eng. News* **2006**, *84*, 30.
(18) Johnson, J. *Chem. Eng. News* **2007**, *85*, 19.
(19) Cleveland, C.; Hall, C. A. S.; Herendeen, R. A. *Science* **2006**, *312*, 1746.
(20) Palsson, B. O.; Faith-Afshar, S.; Rudd, D. F.; Lightfoot, E. N. *Science* **1981**, *213*, 513.
(21) Ng, T. K.; Busche, R. M.; McDonald, C. C.; Hardy, R. W. F. *Science* **1983**, *219*, 4585.
(22) Physorg.com. Science:Physics:Tech:Nano:News. www.physorg.com/news77180879.htm, Georgia Institute of Technology.
(23) Velu, S.; Satoh, N.; Gopinath, C. S.; Suzuki, K. *Catal. Lett.* **2002**, *82*, 145.
(24) Deluga, D. A.; Salge, J. R.; Schmidt, L. D.; Verykios, X. E. *Science* **2004**, *303*, 993.
(25) Velu, S.; Song, C. Advances in Catalysis and processes for hydrogen production from ethanol. In *Catalysis*; Spivey, J. J., Ed.; Royal Society of Chemistry: London, **2007**; Vol. 20, pp 65–106.
(26) Blottnitz, H.; Curran, M. A. *J. Cleaner Prod.* **2007**, *15*, 607.
(27) Prasad, S.; Singh, A.; Joshi, H. C. *Resour. Conserv. Recycl.* **2007**, *50*, 1.
(28) Fougret, C. M.; Holderich, W. F. *Appl. Catal. A: General* **2001**, *207*, 295.
(29) Rostrup-Nielsen, J. R. *Science* **2005**, *308*, 1421.
(30) Gray, K. A.; Zhao, L.; Emptage, M. *Curr. Opin. Chem. Biol.* **2006**, *10*, 141.
(31) Spath, P. L.; Dayton, D. C. *Preliminary Screening - Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas*; NREL/TP-510-34929, National Rewnewable Energy Laboratory: Golden, CO, 2003.

unconverted biomass to ethanol, are being developed.[31,32] However, research on these topics is still in its infancy.

Biomass conversion to mixed alcohol fuels using the "MixAlco" process has been reported recently by Holzapple et al. from Texas A&M University, TX.[33,34] The process involves a combination of biological (fermentation) and chemical (catalytic) transformations for converting biodegradable materials such as sorted municipal solid waste, sewage sludge, industrial biosludge, manure, agricultural residues, etc. into mixed alcohol fuels. The biological process converts biodegradable materials into chemicals such as esters, carboxylic acids, ketones, etc. The biomass feedstock is first treated with lime to increase its digestibility. It is then fed into a fermentor in which a mixed culture of acid-forming microorganisms produces carboxylic acids. Calcium carbonate is added to the fermentor to neutralize the acids to their corresponding carboxylate salt. The dilute (~3%) carboxylate salts are concentrated to 19% using an amine solvent that selectively extracts water. Drying is completed using multieffect evaporators. Finally, the dry salts are thermally converted to ketones which are subsequently hydrogenated to alcohols. H_2 for hydrogenation of ketones may be obtained by gasification of undigested residue in the fermentation process. It appears that the mixed alcohol product of the MixAlco process consists of primarily 2-propanol mixed with higher alcohols up to 7-tridecanol.[33] The process is currently in the pilot-plant stage with a production capacity of 100 lb/day and is expected to expand to a larger plant that will process about 10 ton/d of biomass shortly.

In contrast to the biological process discussed above, the indirect liquefaction consisting of gasification of entire biomass components, including hemicellulose and lignin, into syngas followed by the catalytic conversion of syngas to liquid fuels is known and may be a promising approach for converting biomass into liquid fuels.[35,36] In this route, the biomass components are first gasified to produce a raw syngas containing CO and H_2. Typical syngas compositions obtained from a few selected industrial gasifiers are gathered in Table 1.[37] The syngas from the gasifier is refined by multiple gas cleanup processes to remove contaminants such as H_2S, tars, NH_3, etc. (Figure 1). This process is similar to coal gasification; however, it is operated at a relatively lower temperature because biomass is more reactive than coal. After cleaning, the syngas can be catalytically converted into a wide range of liquid fuels and chemicals as illustrated in Figure 2. Syngas production processes by coal gasification and natural gas reforming, followed by direct conversion of syngas to gasoline, diesel, and waxes by Fischer–Tropsch (FT) synthesis using Fe-based and Co-based catalysts and methanol synthesis using a Cu–ZnO/Al_2O_3 or Cu–ZnO/Cr_2O_3 catalyst, are well established syngas conversion technologies.[31,35,36,38] Methanol obtained from syngas can serve as a building block for the synthesis of a variety of other fuels and chemicals, including dimethyl ether (DME), gasoline, olefins, acetic acid, and formaldehyde.[39,45] The technologies for the conversion of natural gas to liquid products, coal to liquid products, and biomass to liquid products, all via gasification to syngas followed by FT-type catalytic conversions, are referred to as GTL, CTL, and BTL, respectively.

Table 1. Typical Syngas Compostions from Various Industrial Gasifiers[37]

	Lurgi	Purox[a]	Shell
feedstock	bark	MSW[b]	coal
reactor type	CFB[c]	fixed-bed	fluid-bed-entrained flow
H_2 (%)	20.2	23.4	24
CO (%)	19.6	39.1	67
CO_2 (%)	13.5	24.4	4
H_2O (%)	Dry	Dry	3
CH_4 (%)	(in C_{2+})	5.47	0.02
C_{2+} (%)	3.8	4.93	0
tars	<1 g/m^3		0
H_2S (%)	very low	0.05	1
O_2 (%)			0
NH_3 (%)			0.04
N_2 (%)	42.9		1
H_2/CO ratio	1.0	0.6	0.36
heating value (MJ/m^3)	5.8		9.51

[a] Purox process by Union Carbide. [b] MSW = municipal solid waste. [c] CFB = circulating fluidized-bed.

Research on the catalytic conversion of syngas to higher alcohols has been conducted since the beginning of the 20th century.[31,35,36,38,46–52] Substantial research work has been carried out for developing processes to convert syngas to higher alcohols containing a mixture of methanol and isobutanol as precursors for methyl tertiary butyl ether (MTBE), which has been recommended for use as an octane blend in the past. However, because MTBE has been recently phased out and is being replaced by ethanol, the interest in the synthesis of ethanol from biomass- and coal-derived syngas is growing.

The purpose of this paper is to review and critically assess various catalytic processes for the conversion of syngas to ethanol and mixed higher alcohols reported in the recent past with an emphasis on ethanol synthesis, the chemistry and thermodynamics of the processes, the type of catalysts developed and reactors used, and the current status of the technology. Several reviews have been published in the past summarizing the literature on the catalytic conversion of syngas to higher

(32) van Kasteren, J. M. N.; van der Waall, W. R.; Verberne, R. *Bio-ethanol from bio-syngas*; Eindhoven University of Technology (TU/e): Telos, The Netherlands, December 5, 2005.
(33) Holzapple, M. T.; Davison, R. R.; Ross, M. K.; Aldrett-Lee, S.; Adelson, S.; Kaar, W.; Gaskin, D.; Shirage, H.; Chang, N.; Chang, V. S.; Loescher, M. E. *Appl. Biochem. Biotechnol.* **1999**, *79*, 1599.
(34) Holzapple, M. T.; Davison, R. R. Method for conversion of biomass to chemicals and fuels. US Patent 6043392, March 2000.
(35) Rostrup-Nielsen, *Catal. Rev.–Sci. Eng.* **2004**, *46*, 247.
(36) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044.
(37) Ciferno, J. P.; Marano, J. J. *Benchmarking biomass gasification technologies for fuels, chemicals and hydrogen production*; U.S. Department of Energy, National Energy Technology Laboratory: Pittsburgh, PA, June 2002.
(38) Herman, R. G. *Catal. Today* **2000**, *55*, 233.
(39) Lee, S.; Sardesai, A. *Top. Catal.* **2005**, *32*, 197.
(40) Ramos, F. S.; Duarte de Farias, A. M.; Borges, L. E. P.; Monteiro, J. L.; Fraga, M. A.; Sousa, E. F.; Appel, L. G. *Catal. Today* **2005**, *101*, 39.
(41) Hu, J.; Wang, Y.; Cao, C.; Elliott, D. C.; Stevens, D. J.; White, J. F. *Ind. Eng. Chem. Res.* **2005**, *44*, 1722.
(42) Ohno, Y.; Omiya, M. Coal conversion into dimethyl ether as an innovative clean fuel. *12th International Conference on Coal Science*, Cairns, Queensland, Australia, November, 2003.
(43) de Mestier du Bourg, H. Future prospective of DME. *23rd World Gas Conference*, Amsterdam, June, 2006.
(44) Sardesai, A.; Lee, S. *Energy Sources* **2002**, *24*, 301.
(45) Cheung, P.; Bhan, A.; Sunley, G.; Iglesia, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1617.
(46) Xiaoding, X.; Doesburg, E. B. M.; Scholten, J. J. F. *Catal. Today* **1987**, *2*, 125.
(47) Forzatti, P.; Tronconi, E.; Pasquon, I. *Catal. Rev.–Sci. Eng.* **1991**, *33*, 109.
(48) Verkerk, K. A. N.; Jaeger, B.; Finkeldei, C.; Keim, W. *Appl. Catal., A: General* **1999**, *186*, 407.
(49) TSS Consultants. *Grindley ethanol demonstration project utilizing biomass gasification technology: Pilot plant gasifier and syngas conversion testing, August 2002–June 2004*; National Renewable Energy Laboratory and Department of Energy: Golden, CO and Washington, DC, 2005.
(50) Nexant Inc. *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*; DOE-NREL/SR-510-39947, Department of Energy, National Renewable Engergy Laboratory: Golden, CO, May 2006.

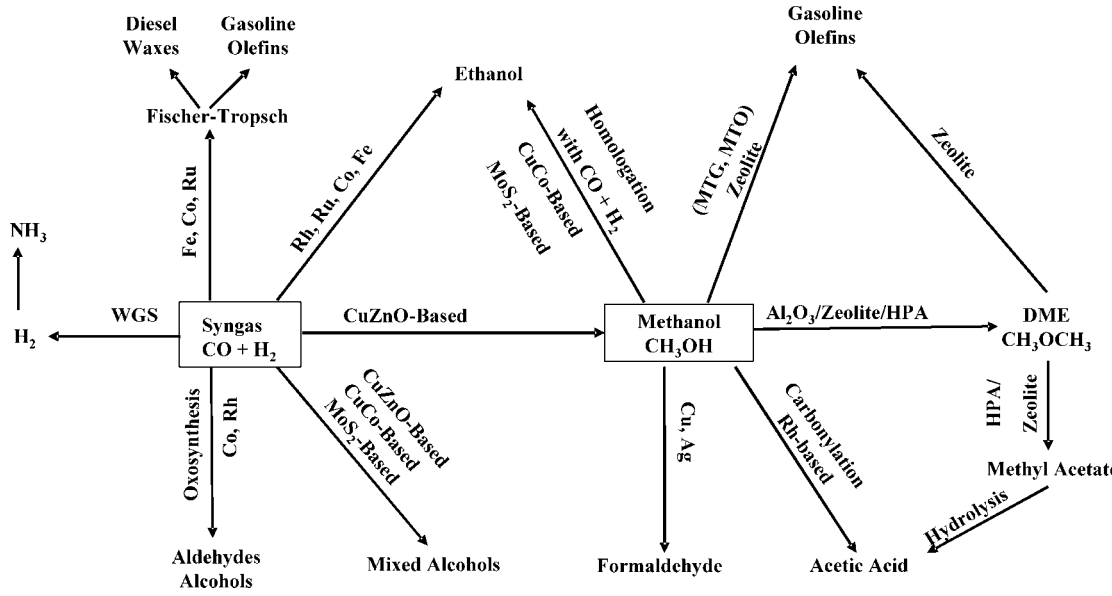

Figure 2. Opportunities for catalytic conversion of syngas to fuels and chemicals: WGS = water–gas shift; MTG = methanol-to-gasoline; MTO = methanol-to-olefin; DME = dimethyl ether; HPA = heteropoly acid.

alcohols, especially for the synthesis of methanol–isobutanol mixtures.[31,35,36,38,46–51] When this paper was under review with the editor of this journal, Spivey and Egbedi[52] published a comprehensive review paper on the catalytic conversion of biomass-derived syngas to ethanol. Yet, the contents discussed in the present review significantly complement, in several parts of the review, that published by Spivey and Egbedi.[52]

2. Historical Perspective and Commercial Status

Alcohols were products of early FT processes; however, the discovery of cobalt- and iron-based FT catalysts that predominantly produced nonoxygenated hydrocarbons for fuels diverted attention away from alcohols. Much of the early development has been on higher alcohol synthesis (HAS), as detailed in a review prepared by scientists from Catalytica Associates, Inc.[53] The only HAS technology that achieved commercialization before 1950 was Farbenindustrie's isobutyl oil process. After the discovery of the Arab oil fields in the late 1940s, technology for alcohol synthesis based on petroleum emerged. The oil embargo of the 1970s provided incentives for renewed interest in the synthesis and utilization of higher alcohols as gasoline blends. A large number of patents were filed on ethanol synthesis and HAS, most notably those by Union Carbide and Sagami Chemical Company on rhodium-based catalysts; Süd-Chemie on copper–zinc-based catalysts; Dow Chemical on sulfided molybdenum-based catalysts; and the Institut Francais du Petrole (IFP) on copper–cobalt-based catalysts.[46,48,53]

When oil prices began to decline after 1985, interest in HAS declined again. None of the HAS catalysts developed to date have been sufficiently active and/or selective to motivate industry to commercialize the process. Consequently, no commercial HAS plants exist today. In contrast, selective synthesis of methanol from syngas is a well-known commercial process due to a very high selectivity that has been achieved.[31,38,46,48] Although not commercialized, a few HAS processes have advanced to the pilot-scale stage, and conceptual processes, based on patented catalytic technologies, have been developed. Some examples are listed in Table 2 and are briefly discussed below.

IFP has filed a number of patents on syngas to higher alcohols conversion using a wide range of mixed oxide catalysts containing Cu, Al, Cr, Mn, Fe, Co, etc., promoted by alkali cations such as Li, Na, K, Cs, Ca, etc.[54] The IFP–Idemitsu process based on Cu–Co alloy catalysts reached the level of a 7000 bbl/y pilot plant in Chiba, Japan.[55] The process scheme used steam reforming of natural gas followed by multiple synthesis reactors and three distillation columns: methanol distillation, extractive distillation with diethylene glycol (DEG), and distillation for DEG recovery. The process produced C_1–C_7 linear mixed alcohols suitable for blending with motor fuels. A heavier alcohols content ranging between 20 and 70 wt % could be obtained under moderate operating conditions, and the purity of the alcohol phase was also very high.

Snamprogetti, Enichem, and Haldor Topsoe (SEHT) jointly developed the SEHT process that used a modified methanol synthesis catalyst.[31] A 400 ton/d pilot plant was constructed and operated between 1982 and 1987. Syngas for this process was produced via partial oxidation of natural gas. Mixed alcohols were synthesized in a series of fixed-bed adiabatic reactors operated in the temperature range between 260 and 420 °C, and pressures as high as 2600–3800 psig. The crude alcohol mixture containing 20% water was purified using three distillation columns. The first distillation column removed methanol and ethanol, the second column removed water, and the third one recovered C_{3+} alcohols by an azeotropic distillation using cyclohexane. The final water content of the product was below 0.1%. The mixed alcohol product was blended at 5 vol % in gasoline that was then marketed successfully as a premium gasoline. However, further research was discontinued because of the availability of large amounts of relatively cheap petroleum.

(51) Phillips, S.; Aden, A.; Jechura, J.; Dayton, D.; Eggeman, T. *Thermochemical ethanol via indirect gasification and mixed alcohol synthesis of lignocellulosic biomass*; DOE-NREL/TP-510-41168, Department of Energy, National Renewable Engergy Laboratory: Golden, CO, April 2007.

(52) Spivey, J. J.; Egbebi, A. *Chem. Soc. Rev.* **2007**, *36*, 1.

(53) Catalytica Associates, Inc. *Synthesis of methanol, glycols, higher alcohols and other oxygenates from CO/H2*; Multiclient study No. 4162, **1983**.

(54) Doan, P. T. Characterization of Cu-Co-Cr-K catalysts. Master's Thesis, Mississippi State University, Mississippi State, MS, August 2001.

(55) Courty, P.; Durant, D.; Sugier, A.; Fremund, E. *Process for manufacturing a mixture of methanol and higher alcohols from synthesis gas*. U.S. Patent 4,659,742, April 1978.

Table 2. Current Status of Selected Catalytic and Combined Catalytic and Fermentation Processes for the Synthesis of Mixed Alcohols

process	overall process scheme	stage of development	scale	comments	ref
IFP–Idemitsu	reform natural gas to syngas; Cu–Co-based modified FT synthesis catalysts; methanol distillation; extractive distillation with diethylene glycol (DEG); DEG recovery	pilot plant	7000 bbl/y	produced C_1–C_7 linear alcohols; higher alcohols between 20 and 70%	54
SEHT	partial oxidation of natural gas to syngas; Cu–Zn-based modified methanol synthesis catalyst; high pressure fixed-bed process; distillation of methanol and ethanol; water distillation; azeotropic distillation for C_{3+} alchols	pilot plant	400 ton/d	crude alcohol mixture contained 20% water; final water content <0.1%; blended (at 5%) to make premium gasoline	31
Lurgi–Octamix	steam and autothermal natural gas reforming; Cu–Zn-based modified methanol synthesis catalyst; low-temperature, low pressure conversion to mixed alcohols; stabilizer column	pilot plant	2 ton/d	process produced mixed alcohols containing 1–2% water	31, 46
Dow Chemical	MoS_2-based catalyst	bench scale			31, 56
Ecalene	syngas with sulfur converted to higher alcohols with nanosized improved MoS_2-based catalyst; 200–300 °C; 500–3000 psig	bench scale	planned scale up to 500 gal/d	higher alcohol yield of >0.4 g/(g catalyst h)	31, 55
MixAlco	fermentation of municipal solid waste into chemicals such as acids, esters, ketones, etc. followed by catalytic hydrogenation of acids; H_2 for hydrogenation is produced by gasification of undigested biomass component	pilot scale	100 lb/d	process produces 2-propanol as major alcohol component; planning to expand the production scale	33, 34

In contrast to SEHT, the Lurgi–Octamix process used a low-pressure, low-temperature modified methanol synthesis catalyst similar to that patented by Süd Chemie, Inc.[31,46] The catalyst used in this process has been reported to contain 25–40 wt % CuO, 10–18 wt % Al_2O_3, 30–45 wt % ZnO, and 3–18 wt % promoter oxide (such as oxides of Cr, Ce, La, Mn, and Th either alone or in combination). Typical operating conditions used in this process were: temperature ≈350 °C, pressure ≈1470 psig, gas hourly space velocity (GHSV) ≈2600 h^{-1}. The process employed syngas with a H_2/CO of 2.0–2.5. Under these operating conditions, the process exhibited a CO conversion of 21–28% with a 66–79% selectivity to alcohol products and 17–25% selectivity to CO_2. Among the alcohol products, the selectivity for methanol was 41–58% and that for ethanol was 1–9% with a total C_{2+} alcohol selectivity ranging from 12 to 24%. The space time yield (STY) of total alcohols was 160–200 mg/(g cat h) in which the C_{2+} alcohols contributed 32–60 mg/(g cat h). A 2 ton/d pilot plant was built in 1990. The process consisted of syngas production via a combination of steam and autothermal reforming of natural gas. Syngas was converted to mixed alcohols with a water content of only 1 to 2%. A stabilizer column was used instead of distillation or molecular sieves to dry the product, unless methanol recovery was desired. The product was granted a U.S. Environmental Protection Agency (EPA) waiver to be used as a gasoline additive in 1988.

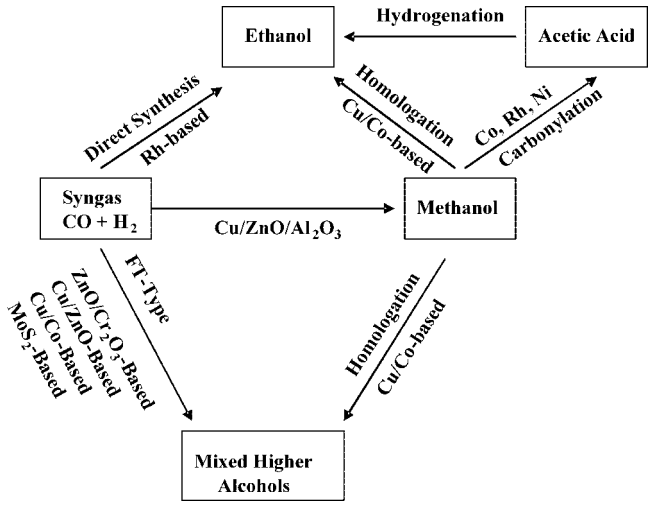

Figure 3. Pathways for the conversion of syngas to ethanol and mixed alcohols.

Both the Dow Chemical and the Ecalene HAS processes use a patented molybdenum sulfide (MoS_2)-based catalyst.[31] The Dow process, first announced in 1984, does not seem to have advanced much beyond the bench scale. Ecalene is a relatively new process that is being developed by Power Energy Fuels, Inc. (PEFI), and is being scaled up to a 500 gal/d pilot plant. It uses a nanosized "improved" MoS_2 catalyst patented by PowerEnerCat., Inc.[56] The Ecalene process requires a small amount of sulfur in the syngas stream or directly added to the reactor vessel. The patent claims a space time yield of higher alcohols greater than 400 mg/(g cat h). The operating conditions are 200–300 °C, with pressures between 500 and 3000 psig.

3. Routes and Chemistry of Syngas Conversion to Ethanol

Syngas as a building block can be converted into ethanol and higher alcohols, either directly or via methanol as an intermedi-

(56) Jackson, G. R.; Mahajan, D. *Method for production of mixed alcohols from synthesis gas*. U.S. Patent 6,248,796, June 19,2001.

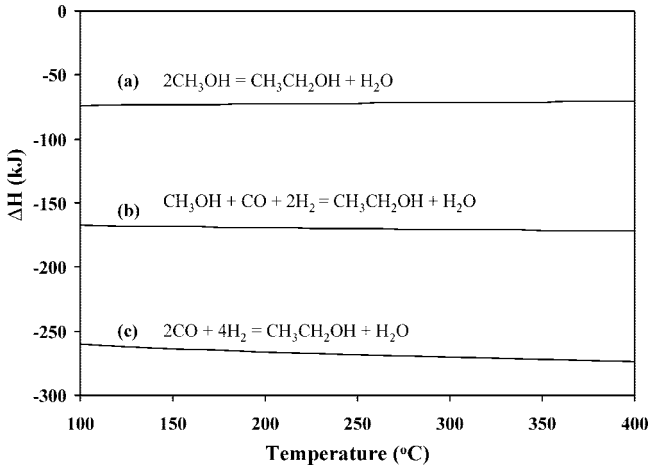

Figure 4. Enthalpy changes in the synthesis of ethanol from syngas via different pathways. (a) Methanol bimolecular reaction. (b) Methanol reductive carbonylation. (c) Direct conversion of syngas to ethanol.

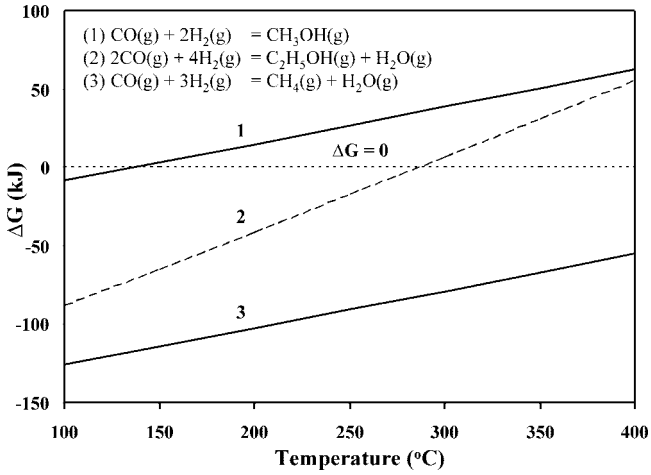

Figure 5. Free-energy changes in the conversion of syngas to methane, methanol, and ethanol.

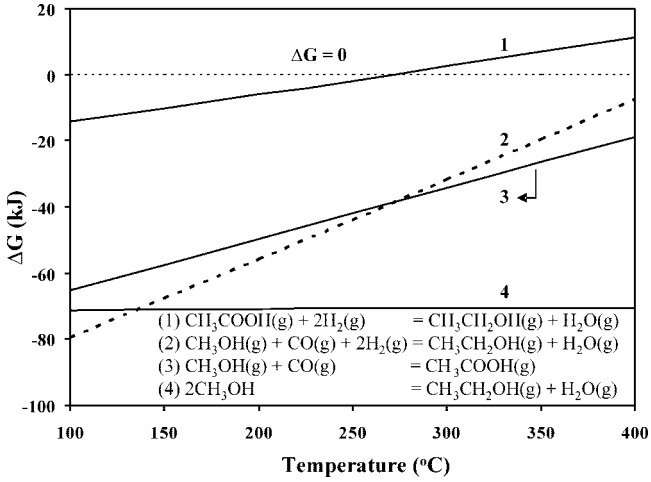

Figure 6. Free-energy changes in the conversion of methanol to ethanol and acetic acid. The free-energy changes for the hydrogenation of acetic acid to ethanol have also been included.

ate, as shown schematically in Figure 3. The reaction network consists of a complex set of numerous reactions, with multiple pathways leading to a variety of products that are impacted by kinetic and thermodynamic constraints. To illustrate the complexity, some of the reactions involved in ethanol and HAS are shown below:

$$CO + 2H_2 \rightarrow CH_3OH \quad \text{(methanol synthesis)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{(water–gas shift)}$$

$$CH_3OH + CO + H_2 \rightarrow CH_3CHO + H_2O \quad \text{(CO beta addition)}$$

$$CH_3OH + CO + 2H_2 \rightarrow CH_3CH_2OH + H_2O \quad \text{(methanol homologation)}$$

$$C_nH_{2n-1}OH + CO + 2H_2 \rightarrow CH_3(CH_2)_nOH + H_2O \quad \text{(HA homologation)}$$

$$2CH_3OH \rightarrow CH_3CH_2OH + H_2O \quad \text{(condensation/coupling)}$$

$$2CH_3OH \rightarrow (CH_3)_2O + H_2O \quad \text{(dehydration/DME formation)}$$

$$(CH_3)_2CO + H_2 \rightarrow (CH_3)_2CHOH \quad \text{(branched iso-alcohols formation)}$$

$$2CH_3CHO \rightarrow CH_3COOCH_2CH_3 \quad \text{(methyl ester formation)}$$

Methanol formation is favored at low temperature and high pressure; however, at high pressures, the formation of HA increases as the temperature increases at the expense of methanol and hydrocarbon formation. To maximize higher alcohol formation, the H_2/CO ratio should be close to the usage ratio, which is about 1. Lower H_2/CO ratios favor CO insertion and C–C chain growth.

At least three different methods are known in the literature for the catalytic conversion of syngas to ethanol and higher alcohols:[31,57]

(i) Direct conversion of syngas to ethanol (eq 1), wherein selective hydrogenation of CO occurs on a catalyst surface to produce ethanol directly.

$$2CO(g) + 4H_2(g) \rightarrow C_2H_5OH(g) + H_2O(g) \quad (1)$$

$$\Delta H^\circ_{298} = -253.6 \text{ kJ/mol of ethanol}$$

$$\Delta G^\circ_{298} = -221.1 \text{ kJ/mol of ethanol}$$

(ii) Methanol homologation, which involves reductive carbonylation of methanol (eq 2) over a redox catalyst surface to make a C–C bond and produce ethanol.

$$CH_3OH(g) + CO(g) + 2H_2(g) \rightarrow C_2H_5OH(g) + H_2O(g) \quad (2)$$

$$\Delta H^\circ_{298} = -165.1 \text{ kJ/mol of ethanol}$$

$$\Delta G^\circ_{298} = -97.0 \text{ kJ/mol of ethanol}$$

(iii) A multistep ENSOL process, wherein syngas is first converted to methanol (eq 3) over a commercial methanol synthesis catalyst followed by methanol carbonylation to acetic acid (eq 4) in the second step and, then, subsequent hydrogenation of acetic acid to ethanol (eq 5) in the third step.[57]

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g) \quad (3)$$

$$\Delta H^\circ_{298} = -90.5 \text{ kJ/mol of ethanol}$$

$$\Delta G^\circ_{298} = -25.1 \text{ kJ/mol of ethanol}$$

$$CH_3OH(g) + CO(g) \rightarrow CH_3COOH(g) \quad (4)$$

$$\Delta H^\circ_{298} = -123.3 \text{ kJ/mol of ethanol}$$

$$\Delta G^{\circ}_{298} = -77.0 \text{ kJ/mol of ethanol}$$

$$CH_3COOH(g) + 2H_2(g) \rightarrow C_2H_5OH(g) + H_2O(g) \quad (5)$$

$$\Delta H^{\circ}_{298} = -41.7 \text{ kJ/mol of ethanol}$$

$$\Delta G^{\circ}_{298} = -19.9 \text{ kJ/mol of ethanol}$$

Among these three routes, both methanol homologation through reductive carbonylation (eq 2) and the ENSOL process have been developed to pilot scale; however, none of them has been commercially practiced yet. The ENSOL process involves multiple steps and employs different types of catalysts, including the traditional Rh-based carbonylation catalyst for the conversion of methanol to acetic acid and a hydrogenation catalyst for the conversion of acetic acid to ethanol. Methanol homologation via reductive carbonylation (eq 2) has been studied; however, ethanol yield and selectivity via this route are lower than commercially accepted levels.

The direct synthesis (eq 1) of ethanol via hydrogenation of CO is the most extensively studied pathway. Depending on the type of catalyst used, both the direct synthesis (eq 1) and the methanol homologation via reductive carbonylation reactions (eq 2) are accompanied by a host of side reactions, as illustrated above, leading to a variety of products, including methane, C_2–C_5 alkanes and olefins, ketones, aldehydes, esters, and acetic acid. Methanation can be particularly significant via hydrogenation of CO (eq 6), which is highly exothermic and consumes a significant amount of H_2:

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) \quad (6)$$

$$\Delta H^{\circ}_{298} = -205.9 \text{ kJ/mol of ethanol}$$

$$\Delta G^{\circ}_{298} = -141.9 \text{ kJ/mol of ethanol}$$

To increase the ethanol yield and selectivity, the catalyst and conditions need to be designed to suppress methanation activity. In addition to various side reactions, the water–gas shift (WGS) reaction (eq 7) always occurs because it is catalyzed by most of the catalysts typically used in syngas conversion to alcohols.

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \quad (7)$$

$$\Delta H^{\circ}_{298} = -41.1 \text{ kJ/mol of ethanol}$$

$$\Delta G^{\circ}_{298} = -28.6 \text{ kJ/mol of ethanol}$$

The WGS reaction is desirable for syngas feed with a low H_2/CO ratio as the reaction generates additional H_2, but it is undesirable for feeds containing a high H_2/CO ratio. The direct synthesis of ethanol and higher alcohols typically requires H_2/CO ratios in the range between 1 and 2. Lower ratios can lead to catalyst deactivation or modification of the active sites via carbon deposition or carbide formation.

4. Thermodynamic Considerations

The changes in enthalpy (ΔH), Gibbs free energy (ΔG), and the equilibrium constant (K_{eqm}) for the conversion of syngas to ethanol via direct synthesis and methanol homologation pathways shown in eqs 1–5 have been calculated in the temperature range between 25 and 400 °C using HSC chemistry software. The thermodynamic data are summarized in Table 3 and compared in Figures 4–6 in the form of Ellingham-type diagrams showing the variation of ΔG and ΔH with respect to temperature. It can be noted from Figure 4 that the direct conversion of syngas to ethanol is highly exothermic (line c), with ΔH ranging between −260 and −270 kJ/mol of ethanol. Cofeeding of methanol along with syngas decreases the exothermicity of the reaction; thus, the ΔH for methanol homologation via reductive carbonylation reaction (line b) varies between −160 and −170 kJ/mol of ethanol and the value further decreases to about −70 kJ/mol of ethanol for the reaction in the absence of syngas wherein 2 mol of methanol undergo coupling or a bimolecular reaction to produce ethanol (eq 8). Although the methanol bimolecular reaction is not well-known in the literature, mechanistic studies using an isotopic tracer technique indicated the possibility for the occurrence of this reaction under the experimental conditions employed in the methanol homologation reaction.[58,59]

$$2CH_3OH(g) \rightarrow C_2H_5OH(g) + H_2O(g) \quad (8)$$

$$\Delta H^{\circ}_{298} = -74.6 \text{ kJ/mol of ethanol}$$

$$\Delta G^{\circ}_{298} = -71.9 \text{ kJ/mol of ethanol}$$

The Gibbs free energy change shown in Figure 5 for the direct conversion of syngas to ethanol (line 2) shows that the reaction is unfavorable above 280 °C and would require elevated pressures to increase ethanol yield. Methanation (line 3) is highly favorable at all temperatures analyzed, but the conversion of syngas to methanol (line 1) is thermodynamically restricted above 150 °C. To overcome thermodynamic and kinetic restrictions, methanol is commercially synthesized at elevated pressures in the range between 40 and 60 atm (440–590 psig) and temperatures between 220 and 290 °C over CuZn-based catalysts.[31,38] It can also be noted from Figure 5 that while syngas conversion to C_1 products, namely, methane and methanol, are practiced commercially, the direct conversion of syngas to C_2 oxygenates such as ethanol, acetaldehyde, and acetic acid are not, even though the formation of these products is thermodynamically feasible. In fact, acetic acid is commercially produced from methanol carbonylation,[60] although some progress has been shown recently in the direct conversion of syngas to acetic acid.[61,62] Thus, the results infer that the C–C bond formation to make ethanol from syngas is thermodynamically favorable but may be kinetically controlled.

Figure 6 displays the variation of ΔG with respect to temperature for methanol homologation reaction through both methanol reductive carbonylation and bimolecular reaction to produce ethanol (line 2 and line 4, respectively). The analyses indicate that the methanol homologation through reductive carbonylation of methanol (line 2) is thermodynamically favorable below 400 °C, whereas the ΔG for the bimolecular reaction remains the same, approximately −70 kJ/mol of ethanol, in the entire temperature range analyzed. This suggests that the later reaction is thermodynamically much more favorable than the reductive carbonylation pathway. Furthermore, increasing pressure should favor the reductive carbonylation reaction because the reaction involves a decrease in the number of moles from 4 to 2. In contrast, since the number of moles of reactants and products remains the same in the methanol bimolecular reaction,

(57) Winter, C. L. *Hydrocarbon Process.* **1986**, *65*, 71.

(58) Xu, M.; Iglesia, E. *J. Catal.* **1999**, *188*, 125.

(59) Nunan, J. G.; Bogdan, C. E.; Klier, K.; Smith, K. J.; Young, C.; Herman, R. G. *J. Catal.* **1988**, *113*, 410.

(60) Yoneda, N.; Kusano, S.; Yasui, M.; Pujado, P.; Wilcher, S. *Appl. Catal. A: General* **2001**, *221*, 253.

(61) Xu, B.; Sun, K.; Zhu, Q.; Sachtler, W. M. H. *Catal. Today* **2000**, *63*, 453.

(62) Chen, W.; Ding, Y.; Jiang, D.; Wang, T.; Luo, H. *Catal. Commun.* **2006**, *7*, 559.

Table 3. Thermodynamic Data for the Conversion of Syngas to Methanol and Ethanol

		thermodynamic parameter		
reaction	temperature (°C)	$\Delta H°$ (kJ/mol)	$\Delta G°$ (kJ/mol)	K_{eqm}
$CO + 2H_2 = CH_3OH$	25	−90.459	−25.118	2.517E+004
	75	−92.514	−13.994	1.258E+002
	125	−94.368	−2.588	2.186E+000
	175	−96.030	9.040	8.836E–002
	225	−97.509	20.844	6.519E–003
	275	−98.817	32.788	7.504E–004
	325	−99.965	44.845	1.212E–004
	375	−100.966	56.991	2.551E–005
	400	−101.415	63.092	1.270E–005
$2CO + 4H_2 = C_2H_5OH + H_2O$	25	−255.543	−122.096	2.469E+021
	75	−259.077	−99.430	8.303E+014
	125	−262.190	−76.284	1.020E+010
	175	−264.923	−52.769	1.416E+006
	225	−267.313	−28.967	1.091E+003
	275	−269.391	−4.941	2.957E+000
	325	−271.187	19.263	2.078E–002
	375	−272.729	43.606	3.058E–004
	400	−273.413	55.821	4.657E–005
$CH_3OH + CO + 2H_2 = C_2H_5OH + H_2O$	25	−165.085	−96.978	9.808E+016
	75	−166.564	−85.436	6.598E+012
	125	−167.822	−73.696	4.669E+009
	175	−168.893	−61.809	1.603E+007
	225	−169.803	−49.811	1.673E+005
	275	−170.573	−37.729	3.941E+003
	325	−171.222	−25.582	1.715E+002
	375	−171.763	−13.385	1.199E+001
	400	−171.998	−7.271	3.667E+000
$2CH_3OH = C_2H_5OH + H_2O$	25	−74.626	−71.860	3.896E+012
	75	−74.050	−71.441	5.243E+010
	125	−73.454	−71.108	2.136E+009
	175	−72.863	−70.849	1.814E+008
	225	−72.294	−70.655	2.566E+007
	275	−71.756	−70.517	5.252E+006
	325	−71.256	−70.426	1.415E+006
	375	−70.797	−70.376	4.700E+005
	400	−70.583	−70.364	2.887E+005

the reaction should be independent of pressure. However, the reverse reaction to produce syngas by methanol decomposition (eq 9) could also occur as the reaction becomes favorable above 150 °C and atmospheric pressure.

$$CH_3OH(g) \rightarrow CO(g) + 2H_2(g) \quad (9)$$

$$\Delta H^{\circ}_{298} = +25.1 \text{ kJ/mol of ethanol}$$

$$\Delta G^{\circ}_{298} = +90.5 \text{ kJ/mol of ethanol}$$

The free-energy change for methanol reductive carbonylation is close to that of the methanol carbonylation to acetic acid (Figure 6, line 3). The commercial Monsanto process for methanol carbonylation to acetic acid is being operated in the temperature range between 180 and 220 °C and in the pressure range between 30 and 40 atm (440–600 psig) and exhibits a high selectivity to acetic acid based on methanol (99%) and carbon monoxide (85%).[60] The ENSOL process for the synthesis of ethanol described above in section 3.0 also involves the synthesis of acetic acid via methanol carbonylation and subsequent hydrogenation of acetic acid to ethanol.[57] However, the free-energy change for the hydrogenation of acetic acid to ethanol (line 1) approaches equilibrium at about 270 °C, indicating that this reaction is thermodynamically restricted at higher temperatures and that the reaction should be performed at lower temperatures.

Figure 7 and 8 show the equilibrium compositions and CO conversions in direct hydrogenation of CO to ethanol and methanol homologation to ethanol, respectively. These data were calculated at 600 psig (around 42 bar) pressure for an inlet H_2/CO ratio of 2. The results indicate that a CO conversion between 60 and 70 mol % with 40–45 mol % ethanol could be obtained in both reactions below 350 °C. Both CO conversion and ethanol composition decrease with further increasing temperature, suggesting that these reactions should be performed below 350 °C. The data shown in Figure 8 indicate that, in the methanol reductive carbonylation reaction, a complete conversion of methanol could be obtained at all temperatures. However, the CO conversion approaches 0 around 400 °C and exhibits negative conversion values with further increasing temperature. This is because of the decomposition of methanol to CO and H_2 (eq 9) at high temperatures, as discussed above.

5. Catalysts

Syngas conversions to ethanol via direct synthesis and methanol homologation pathways have been performed using a wide range of homogeneous and heterogeneous catalysts. However, before discussing the results of these catalysts, the desired performance is put into perspective based on the manufacture of methanol. Syngas conversion to the simplest alcohol, methanol, using a Cu–ZnO/Al_2O_3 or Cu–ZnO/Cr_2O_3 catalyst operating at 220–290 °C and 40–60 atm, is a well-established technology.[38,46] The so called low-temperature methanol synthesis process using these catalysts has essentially replaced the older high-temperature process that operated at 150 atm (2204 psig) and 400 °C using a Cu-free "zinc-chromite-type" (ZnO/Cr_2O_3) catalyst. The copper-based catalysts produce methanol with a selectivity of about 99%, boast a life of about 4 years without need for regeneration, and produce methanol at a rate of 1.3–1.5 g/(g cat h). This performance and space time yield (STY) of the methanol

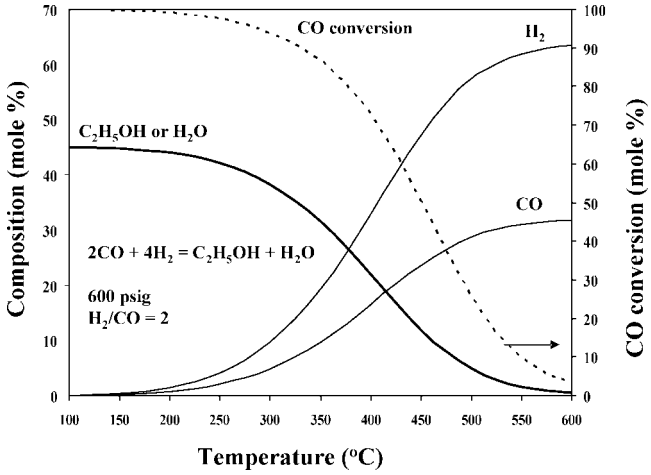

Figure 7. Equilibrium compositions for the direct synthesis of ethanol via hydrogenation of CO.

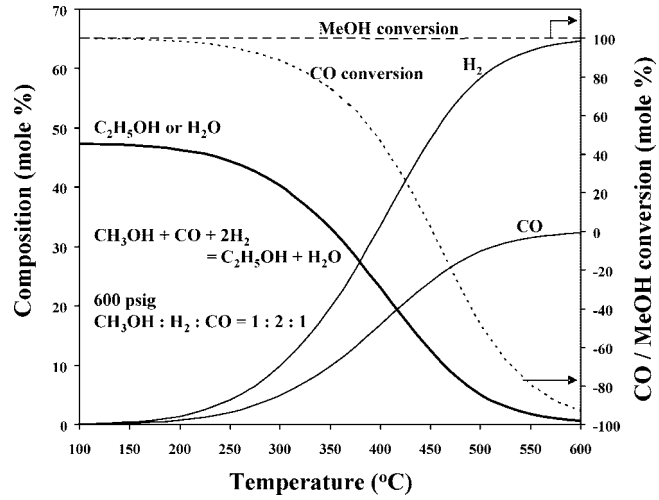

Figure 8. Equilibrium compositions for the synthesis of ethanol via methanol reductive carbonylation.

synthesis catalytic process could serve as a benchmark for the catalytic conversion of syngas to ethanol and higher alcohols discussed in this review.

5.1. Homogeneous Catalysts. Reactions of syngas in homogeneously catalyzed solutions containing Co, Ru, or Rh metal complexes directly produce ethanol and C_2 oxygenates from syngas.[63–66] Certain oxy-solvents (such as glymes, *N*-methlpyrrolidine, sulfolane, and acetic acid), iodide, or ionic liquids (such as Bu_4PBr) have been used as promoters. A process has been reported for producing methanol, ethanol, and methane using triruthenium dodecacarbonyl as a catalyst dissolved in tripropylphosphine oxide with iodine as a promoter.[63,66] The ethanol yield was only 46 g/(L cat h) at 240 °C and 4000 psig. Researchers from the Texaco Company have reported a process for converting syngas to alcohol-ester fuels using a RuO catalyst mixed with Bu_4PI quaternary salt.[66] They have obtained about 60% selectivity to ethanol at 220 °C and 6320 psig.

Methanol homologation to ethanol using homogeneous catalysts has also been reported by Wender et al. in 1951.[67] Using the catalyst $[Co(CO)_4]_2$, the authors have demonstrated the formation of about 39% ethanol from methanol and syngas at 180 °C and 4560 psig. Following this early work, the reaction has been studied extensively using various Co, Ru, or Co–Ru bimetallic complexes. The higher hydrogenation capability of Ru in the Co–Ru bimetallic complexes improves the selectivity to ethanol. The reaction in the later reports has been performed in the temperature range between 160 and 250 °C and pressure range between 200 and 5000 psig. Some of this earlier work used iodine or iodide promoters, as reported in the review by Catalytica, Inc.[53] Depending upon the type of catalyst and promoter used, a methanol conversion between 10% and 100% with ethanol selectivity up to 90% has been reported. Acetates, higher alcohols, and methane were produced as byproducts. Among the catalysts studied, RuO_2–*n*-Bu_4PBr–CoI_2 showed about 56% ethanol selectivity, with about 80% methanol conversion at 200 °C and 4000 psig.[66] The methanol conversion and ethanol selectivity have been improved further by the addition of quaternary phosphonium or ammonium base.

Researchers from Argonne National Laboratory, USA, have recently reported a novel selective catalytic ethanol synthesis route.[68] The process incorporates (1) steam reforming of biomass such as switch grass to produce syngas, (2) methanol synthesis using the commercial heterogeneous Cu/ZnO catalyst, and (3) carbonylation followed by hydrogenation of methanol using a $HFe(CO)_4$ complex as a homogeneous catalyst. The process operates in the temperature range between 180 and 220 °C and at pressures up to 300 atm (over 4400 psig). The rate-determining step in the catalytic reaction has been reported to be the nucleophilic attack of the iron carbonyl complex on 1-methyl-2-pyrrolidinone solvent used for the CO insertion reaction. The process has been reported to produce relatively pure ethanol without coproducing either water or other alcohols. The overall process has been denoted as shown in eq 1010.

$$CH_3OH(g) + 2CO(g) + H_2(g) \rightarrow C_2H_5OH(g) + CO_2(g) \quad (10)$$

$$\Delta H^\circ_{298} = -206.2 \text{ kJ/mol of ethanol}$$

$$\Delta G^\circ_{298} = -125.6 \text{ kJ/mol of ethanol}$$

The reaction according to eq 10 produces "dry ethanol" rather than a mixture of ethanol and water produced in the conventional methanol homologation reaction. If successfully developed, this process could become economical because it avoids the tedious separation step employed for recovering ethanol from an ethanol–water azeotropic mixture. Also, the process uses a non-noble metal-based catalyst, which could be cost effective. However, the handling of the toxic $Fe(CO_4)$ complex and the use of high pressure (over 4000 psig) are some of the major concerns for the practical application and commercial viability of this process.

5.2. Heterogeneous Catalysts. The heterogeneous catalysts employed for the synthesis of ethanol and higher alcohols can be broadly classified into two categorires: (i) noble metals-based and (ii) Non-noble metals-based. The noble metals-based catalysts are primarily supported rhodium (Rh) catalysts while the non-noble metals-based catalysts include modified methanol synthesis catalysts, modified Fischer–Tropsch synthesis catalysts, and MoS_2-based catalysts. These catalysts have been employed for the synthesis of higher alcohols by at least two different pathways: namely, (a) direct conversion of syngas, wherein both

(63) Maitlis, P. M. J. *Mol. Catal. A: Chemical* **2003**, *204–205*, 55.
(64) Dombeck, B. D. *J. Organomet. Chem.* **1983**, *250*, 467.
(65) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1.
(66) Lin, J.-J.; Knifton, J. F. *Synthesis of ethanol by homologation of methanol*. U.S. Patent 4,374,285, 1983.
(67) Wender, I,; Friedel, R. A.; Orchin, M. *Science* **1951**, *113*, 206.
(68) Rathke, J. W.; Chen, M. J.; Klinger, R. J.; Gerald, R. E.; Marshall, C. L.; Rodgers, J. L. *Proceedings of the 2006 Meetings of the DOE/BES Catalysis and Chemical Transformations Program*, Cambridge, MD, May 21–24, 2006.

noble metals-based and non-noble metals-based catalysts have been employed and (b) methanol homologation in which mostly non-noble metals-based catalysts have been employed. Consequently, the type of catalysts used in ethanol and higher alcohols synthesis in this section are discussed under these two different pathways. While the noble metals-based catalysts produced mainly ethanol and other C_2-oxygenates, the non-noble metals-based catalysts favored the formation of a spectrum of mixed alcohols ranging from at least C_1–C_6 with more selectivity toward methanol and isobutanol. Hence, although this review focuses mainly on ethanol synthesis, the contents discussed here are also applicable in general to the synthesis of mixed higher alcohols and other C_{2+}-oxygenates from syngas.

5.2.1. Direct Conversion of Syngas to Ethanol and Higher Alcohols. A wide range of noble metals-based and transition metals-based supported catalysts have been employed in the direct conversion of syngas to ethanol and higher alcohols. Noble metals such as Rh, Ru, and Re supported on Al_2O_3, SiO_2, etc. have been reported. Among them, Rh-supported catalysts have been studied extensively as these catalysts produced C_{2+}-oxygenates with a high selectivity toward ethanol. The non-noble metals-based catalysts have been employed for HAS (C_{2+}-alcohols), particularly isobutanol. The types of catalysts used and their catalytic performances are discussed below in detail. Since different authors have reported the yields and selectivities of the products differently, the authors attempted to recalculate and compare them in the same way.

5.2.1.1. Noble Metals-Based Catalysts. 5.2.1.1.1. Catalytic Activity and Selectivity. The direct conversion of syngas to ethanol and other C_2-oxygenates has been reported by Union Carbide Company as early as 1975 over SiO_2-supported Rh catalyst promoted by metal ions, such as Fe, Mo, Mn, W, Th, and U, in a stirred autoclave reactor.[53,69,70] The best results were obtained over a catalyst containing 2.5% Rh supported on SiO_2 and promoted by 0.05 wt % Fe. At 300 °C and 1030 psig using H_2/CO, the catalyst produced 49% methane, 2.8% methanol, 31.4% ethanol, and 9.1% acetic acid. However, the rates of methanol and ethanol production were about 50 g/L cat h).

Following this early work, there are several reports on the conversion of syngas to ethanol and other C_{2+}-oxygenates using a wide range of noble metals-based catalysts containing Rh, Ru, and Re supported on various oxides, such as SiO_2, Al_2O_3, CeO_2, ZrO_2, MgO, etc.[53,71–90] These studies have focused on investigating the effect of nature of promoters and supports on the catalytic activity and selectivity for ethanol formation in a fixed-bed reactor. Holy and Carey,[72] using a Co–Fe–Rh/SiO_2 catalyst with a Co:Fe:Rh atomic ratio of 2.6:2.5:3.7, obtained a moderately high ethanol selectivity of about 30% at a CO conversion of about 6% at 278 °C and 900 psig using a H_2/CO ratio of about 1. Under these operating conditions, the reaction also produced a significant amount of methanol (25.3%) and propanol (24.9%). Yu-Hua et al.[77] have investigated the promoter effect of rare earth oxides (REO), such as La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, and Sm_2O_3, on the catalytic performance of Rh/SiO_2 catalyst containing 2 wt % Rh and 4.5 wt % REO in the hydrogenation of CO using a H_2/CO ratio of 1.69 in a fixed-bed reactor. At 220 °C and atmospheric pressure, the catalysts containing CeO_2 and Pr_6O_{11} as promoters produced C_2 oxygenates with a high selectivity (about 48%) toward ethanol. According to these authors, the added promoter covers a part of the Rh metal, thereby suppressing the H_2 chemisorption activity of Rh and creating new catalytic active sites at the Rh–REO interface. During the catalyst prereduction, the H_2 chemisorbed on Rh particles spills over onto the promoter and partially reduces it, releasing a suboxide of the REO at the Rh–REO interface, which then wets the Rh particles through metal–metal bonding and oxide bridging and spreads out across the surface of Rh particles. The partially exposed cationic center or oxygen vacancy of the reduced REO acts as a Lewis acid center or an oxophilic center to coordinate or interact by charge–dipole interaction with the oxygen end of μ_2-ligated CO adsorbed on the Rh active site for dissociation or insertion of CO to form C_{2+}-oxygenates.

Gronchi et al.[79] have investigated the effect of Rh dispersion on V_2O_5 and ZrO_2 on CO conversion and ethanol selectivity at 220 °C and atmospheric pressure. They used a Rh loading between 0.2 and 1.0 wt % on V_2O_5 and ZrO_2 to adjust the Rh dispersion. It has been observed that in the low-temperature range (below 230 °C), as the Rh particle size increases, the fraction of active sites capable of CO insertion also increases. As a consequence, a high selectivity to ethanol rather than CO_2 is observed. The 1% Rh/V_2O_5 catalyst offered an ethanol selectivity of about 37% at a CO conversion of 4.5%. Unfortunately, the reaction also produced high selectivity (>50%) to C_1–C_4 hydrocarbons, which are undesirable.

Burch and Hayes[81] have studied the syngas conversion to ethanol reaction over catalysts containing 2 wt % Rh and 0–10 wt % Fe_2O_3 supported on Al_2O_3 catalyst in a fixed-bed reactor at 270 °C and 145 psig. They observed that the addition of Fe_2O_3 greatly suppresses CH_4 formation with concomitant increase in the selectivity to ethanol. The catalyst containing 2 wt % Rh and 10 wt % Fe exhibited a maximum ethanol selectivity of about 50%. The authors noted that the close interaction between metal and promoter leads to an increased Rh–promoter interface, which accommodates chemisorbed CO that is carbon-bound to the Rh atom and oxygen-bound to the promoter ion. According

(69) van der Lee, G.; Schuller, B.; Post, H.; Favre, T. L. F.; Ponec, V. *J. Catal.* **1986**, *98*, 522.
(70) Ehwald, H.; Ewald, H.; Gutschick, D.; Hermann, M.; Miessner, H.; Ohlmann, G.; Schierhorn, E. *Appl. Catal.* **1991**, *76*, 153.
(71) Takeuchi, K.; Matsuzaki, T.; Arakawa, H.; Sugi, Y. *Appl. Catal.* **1985**, *18*, 325.
(72) Holy, N. L.; Carey, T. F. *Appl. Catal.* **1985**, *19*, 219.
(73) Underwood, R. P.; Bell, A. T. *Appl. Catal.* **1986**, *21*, 157.
(74) Bowker, M. *Catal. Today* **1992**, *15*, 77.
(75) de Jong, K. P.; Glezer, J. H. E.; Kuipers, H. P. C. E.; Knoester, A.; Emeis, C. A. *J. Catal.* **1990**, *124*, 520.
(76) Ponec, V. *Stud. Surf. Sci. Catal.* **1991**, *64*, 117.
(77) Yu-Hua, D.; De-An, C.; Khi-Rui, T. *Appl. Catal.* **1987**, *35*, 77.
(78) Ichikawa, M.; Fukushima, T.; Yokoyama, T.; Kosugi, N.; Kuroda, H. *J. Phys. Chem.* **1986**, *90*, 1222.
(79) Gronchi, P.; Tempesti, E.; Mazzocchia, C. *Appl. Catal. A: General* **1994**, *120*, 115.
(80) Lin, P.-Z.; Liang, D.-B.; Lou, H.-Y.; Xu, C.-H.; Zhou, H.-W.; Huang, S.-Y.; Lin, L.-W. *Appl. Catal. A: General* **1995**, *131*, 207.
(81) Burch, R.; Hayes, M. J. *J. Catal.* **1997**, *165*, 249.
(82) Izumi, Y.; Kurakata, H.; Aika, K. *J. Catal.* **1998**, *175*, 236.
(83) Wang, Y.; Lou, H.; Liang, D.; Bao, X. *J. Catal.* **2000**, *196*, 46.
(84) Luo, H. Y.; Zhang, W.; Zhou, H. W.; Huang, S. Y.; Lin, P. Z.; Lin, L. W. *Appl. Catal. A: General* **2001**, *214*, 161.
(85) Ojeda, M.; Granados, M. L.; Rojas, S.; Terreros, P.; Garcia-Garcia, F. J.; Fierro, J. L. G. *Appl. Catal. A: General* **2004**, *261*, 47.
(86) Ichikawa, M.; Shikakura, K.; Kawai, M. Heterogeneous Catalysis Related to Energy Problems. *Proceedogs of Symposium*, Dalian, China, 1982.
(87) Matsuzaki, T.: Takeuchi, K.; Hanaoka, T.; Arawaka, H.; Sugi, Y. *Appl. Catal. A: General* **1993**, 105, 159.
(88) Hu, J.; Wang, Y.; Cao, C.; Elliott, D. C.; Stevens, D. J.; White, J. F. *Catal. Today* **2007**, *120*, 90.
(89) Hu, J.; Dagle, R. A.; Holladay, J. D.; Cao, C.; Wang, Y.; White, J. F.; Elliott, D. C.; Stevens, D. J. Alcohol synthesis from CO or CO_2. *US Patent application publication No. US2007/0161717*, July 2007.
(90) Marengo, S.; Martinengo, S.; Zanderighi, L. *Symposium on octane and cetane enhnacement processes for reduced-emissions moter fuels. Presented before the ACS-Dvision of Petroleum Chemistry*,San Francisco, April 5–10, 1992.

Table 4. Selected Rh-Based Supported Catalysts Employed in the Direct Conversion of Syngas to Ethanol

	experimental conditions					carbon selectivity (%)[b]					alc. STY (mg/(g cat h)		
catalyst	temp (°C)	press (psig)	GHSV (h^{-1})	H_2/CO	X_{CO}[a] (%)	HC[c]	CO_2	C_1-OH	C_2-OH	C_{3+}-OH	EtOH	$\Sigma_{alcohol}$	ref
$RhCoFeK/SiO_2$[d]	281	900	3000	1.0	6.8	41.9	14.7	8.6	15.8	18.7	NA	NA	72
$RhCe/SiO_2$	350	1 atm	300	1.7	NA	50.9	NA	3.0	45.0	NA	NA	NA	77
$RhMo/ZrO_2$[e]	210	300	2400	1.0	10	34.0	20.0	NA	16.0	NA	NA	NA	90
$1\%Rh/V_2O_5$	220	1 atm	NA	1.0	4.5	50.5	6.0	6.2	37.2	NA	NA	NA	79
$1\%Rh/ZrO_2$	220	1 atm	NA	1.0	2.0	31.5	2.3	15.4	50.8	NA	NA	NA	79
$1\%Rh\text{-}SmV/SiO_2$	280	435	13000	2.0	5.4	38.9	NA	10.6	28.9	1.7	NA	NA	84
$6\%Rh1.5\%Mn/SiO_2$[e,f]	300	783	3750	2.0	40.5	48.1	3.4	1.9	44.5	NA	NA	NA	88

[a] X_{CO} = CO conversion; HC = total hydrocarbons including methane; C_1-OH = methanol; C_2-OH = ethanol; C_{3+}-OH = all the alcohol products except methanol and ethanol; alc STY = space time yield of alcohol; $\Sigma_{alcohol}$ = sum of all the alcohols; NA = data not available. [b] Carbon selectivity is defined as the selectivity of all the carbon-containing products formed from converted carbon, and the values are recalculated from the original reported data. They may be CO_2-free if CO_2 data are not available (NA). [c] HC = hydrocarbon selectivity calculated from the alcohol selectivity data. This may include CO_2 selectivity. [d] Other products include C_2–C_6 aldehydes and esters. [e] Other products are oxygenates. [f] A microchannel reactor was used while others used a fixed-bed reactor.

to the authors, this mode of CO adsorption is paramount in the catalytic synthesis of oxygenates from CO/H_2 mixtures.

Lin et al.[80] have employed Mn as a promoter to 1% Rh/SiO_2 catalyst with a Rh/Mn weight ratio of 1 and performed the CO hydrogenation at 310 °C and 870 psig continuously for about 1000 h. Under the experimental conditions employed, the catalyst exhibited a high selectivity of 34.8% for ethanol, 30.7% for acetic acid, and 19.2% for acetaldehyde. The selectivities for other oxygenates were significantly lower. However, the authors have not reported the CO conversion levels. Ojeda et al.[85] used Al_2O_3 as a support instead of SiO_2 and evaluated a series of $RhMn/Al_2O_3$ catalysts containing 3 wt % Rh while varying the Mn loading between 0 and 3.2 wt % in the CO hydrogenation reaction at 260 °C and 290 psig. The selectivity for oxygenate was about 50%, with ethanol being the major oxygenate. The authors have noted that the main effect of Mn addition was to promote or suppress the formation of ethanol with no significant effect on the other oxygenated compounds. The authors have also noted that ethanol and acetaldehyde are formed by different reaction pathways.

Luo et al.[84] have reported that Sm and V promoted Rh catalysts supported on SiO_2 are highly selective to ethanol. At 280 °C, 435 psig, and at a gas hourly space velocity (GHSV) of 13 000 h^{-1}, they obtained about 30% ethanol selectivity at a CO conversion of about 5%. According to these authors, V can be easily reduced to a lower valence state, and this state has high capacity of adsorbing and storing H_2. These lower valent vanadium species possess a strong ability for hydrogenation.

The use of Rh-based catalysts for the synthesis of higher alcohols, especially ethanol, has been known as early as 1978 when Ichikawa et al.[86] demonstrated the formation of ethanol with high yields over Rh clusters supported on weekly basic oxides such as La_2O_3, Cr_2O_3, TiO_2, and ThO_2. Strongly basic supports such as MgO and ZnO yielded methanol as a major product, whereas acidic supports such as Al_2O_3, V_2O_5, SnO_2, and WO_3 produced methane and higher hydrocarbons. Table 4 summarizes the results of a few Rh-based catalysts tested in the conversion of syngas to ethanol.

Figure 9 shows the effect of promoter type on the catalytic activity and selectivity for ethanol formation over Rh-supported SiO_2 catalysts.[76,86] As can be seen, promoters such as Zr, Ti, and V exhibit higher catalytic activity for ethanol formation, whereas La, Ce, and Y show higher ethanol selectivity. The addition of a second promoter, such as Li, Na, and K, further improved the selectivity toward C_2-oxygenates by suppressing the hydrocarbon selectivity. Promoters such as Cr, Mn, Zn, etc. exhibit poor ethanol productivities and selectivities. However, Mn-promoted Rh catalysts have been recently reported to be potential catalysts for syngas conversion to ethanol and

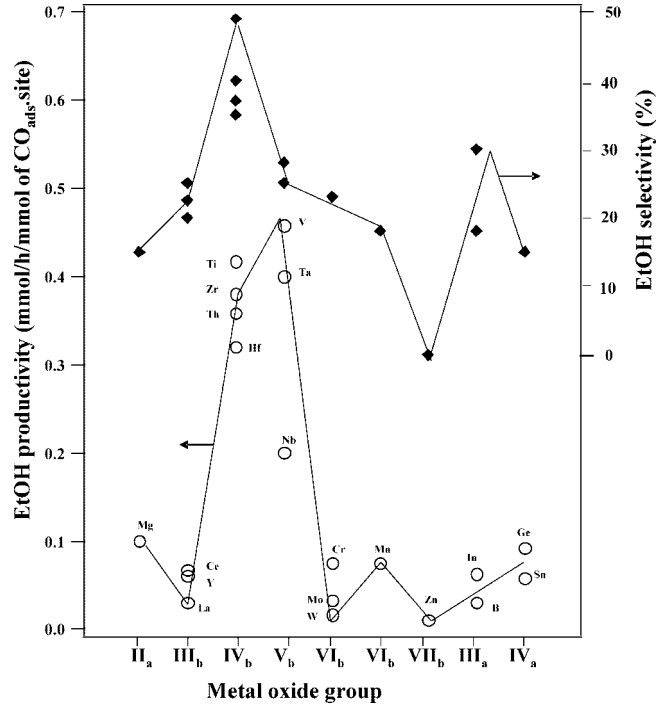

Figure 9. Effect of the nature of the promoter on catalytic activity and selectivity for ethanol from syngas over Rh/SiO_2 catalysts.

C_{2+}-oxygenates.[85,87,88] Higher selectivity toward ethanol has been observed over Li- or Na-containing Mn-promoted Rh/SiO_2 catalyst.[78,86]

In addition to the catalyst compositions, the reaction operating conditions also play an important role in catalytic activity and ethanol selectivity. Recently, Hu et al.[88,89] employed a microchannel reactor containing $Rh–Mn/SiO_2$ catalyst for the conversion of biomass-derived syngas to alcohols and C_2-oxygenates. The reaction was performed in the temperature range between 265 and 300 °C and pressure between 550 and 800 psig using a H_2/CO ratio of 2 and GHSV of 3750 h^{-1}. The reaction under these operating conditions produced a mixture of CH_4, CO_2, methanol, ethanol, and C_{2+}-hydrocarbons and oxygenates, with methane and ethanol being the major products. The authors have observed that increasing reaction temperature from 280 to 300 °C increased the CO conversion from about 25 to 40%, but the selectivity to methane, the undesirable byproduct, also increased from about 38 to 48%. They have noted that reaction temperature, rather than reaction pressure, has a strong influence on the product selectivity. When the H_2/CO ratio was reduced from 2 to 1, the CO conversion also dropped. This also decreased the ethanol selectivity and increased C_{2+}-hydrocarbons. The

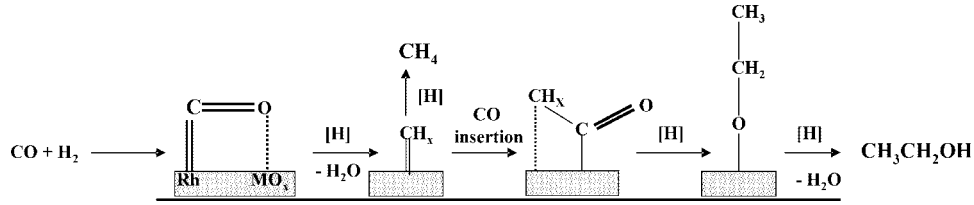

Figure 10. Simplified mechanism for the conversion of syngas to ethanol over Rh-based catalysts.

catalytic performance was also compared after standard prereduction and redox cycle treatment that involves successive reduction and oxidation steps. Improvements in catalytic activity were found in the later treatment due to an improved Rh metal dispersion on the support. The Rh–Mn/SiO_2 catalyst at 300 °C, 783 psig pressure, and 3750 h^{-1} GHSV exhibited about 40% CO conversion, with an ethanol selectivity of about 44%. However, the ethanol yield obtained in these experiments has not been reported.

5.2.1.1.2. Reaction Mechanism. The mechanism of ethanol formation over Rh-based catalysts involves adsorption of CO, which is carbon-bound to the Rh atom and oxygen-bound to a promoter ion.[81,83] A close interaction between Rh and the promoter ion has been reported to be important to achieve this mode of adsorption. The geometrical structure of the active site has been proposed to be ($Rh_x^0Rh_y^+$)–O–M^{n+} wherein a part of Rh is present as Rh^+ and the promoter ion (M^{n+}) is in close contact with these Rh species. The adsorbed CO is then hydrogenated to form an adsorbed –CH_x– species, which is then inserted into adsorbed CO. Hydrogenation of these adsorbed species leads to the formation of ethanol as shown in Figure 10.

Ethanol formation through an acetate mechanism (formation of acetaldehyde followed by reduction) has also been known over Rh-based catalysts promoted by Mn.[83] According to these authors, ethanol is formed by the direct hydrogenation of the tilt-adsorbed CO molecules, followed by CH_2 insertion into the surface CH_2–O species to form an adsorbed (ethylene oxide-type) intermediate. Subsequent hydrogenation of the CH_2–O intermediate species produces ethanol. On the other hand, acetaldehyde is formed through CO insertion into the surface CH_3–Rh species followed by hydrogenation. The role of the promoters according to these authors is to stabilize the intermediate of the surface acetyl species.

On the basis of these mechanisms, it appears that tailoring Rh metal and a promoter ion to achieve a better Rh–promoter ion interaction is the key to producing ethanol selectively by the insertion of adsorbed –CH_2– species rather than acetate formation. The catalytic performance may be further improved by modifying the catalyst composition and the preparation conditions as well as the reaction operating conditions. Because ethanol synthesis is a highly exothermic reaction, better temperature control could substantially improve the ethanol yield and selectivity as suggested by Hu et al.[88,89] based on their evaluation in a microchannel reactor.

Although Rh-based catalysts show promise, exhibiting high selectivity to ethanol and C_{2+}-oxygenates, the commercial viability of these catalysts is questionable because the availability of Rh is limited to about 20 ton/y at present, and over 70% of the available Rh is already being consumed by the automobile industry for making three-way autoexhaust catalysts. As the availability of Rh shrinks, its cost keeps increasing. At present, Rh is being sold at the cost of about $5000/ounce (U.S.). The cost of other noble metals such as Ru, Re, Pd, etc. has also increased significantly in recent years. Consequently, non-noble metals-based catalysts (either methanol synthesis catalysts, Fischer–Tropsch synthesis catalysts, or MoS_2-based catalysts), after suitable modifications to improve the yield and selectivity for ethanol, could become industrially viable catalyst candidates. As stated above in section 2, most of the pilot plant evaluations for the synthesis of higher alcohols in the past used non-noble metals-based catalysts. However, they have not been commercialized because of the poor yield and selectivity of desired alcohol products. The performances of these catalysts and the current status are discussed in the following sections.

5.2.1.2. Non-Noble Metal-Based Catalyst. 5.2.1.2.1. Catalyst Type. Mixed higher alcohols containing a small amount of ethanol have been synthesized from syngas over a wide range of catalysts containing non-noble metals. These catalysts are generally doped with alkali metals such as K or Cs to catalyze the aldol-type condensation reaction[31,38,46–53,91] and can be broadly divided into the following types:

- modified high-temperature and low-temperature methanol synthesis catalysts based on ZnO/Cr_2O_3, Cu–ZnO/Al_2O_3, respectively;
- modified Fischer–Tropsch synthesis catalysts based on Co, Fe, and Ru;
- modified unsulfided Mo-based catalysts;
- modified MoS_2-based catalysts.

Studies using these catalysts produced a mixture of alcohols, especially a mixture of methanol and isobutanol with a little selectivity to ethanol. In fact, in most of these studies, either the selectivity/yield of methanol and isobutanol or the total C_{2+}-alcohols have been reported. The authors of this review identified only a few studies that dealt with the effect of catalyst compositions on ethanol yield and selectivity. These are discussed below.

a. Modified Methanol Synthesis Catalysts. Two different types of methanol synthesis catalysts have been employed industrially. One is Cu-free ZnO/Cr_2O_3 high-temperature methanol synthesis catalyst, and the other is Cu/ZnO-based low-temperature methanol synthesis catalyst.[31,38,91–100] The formation of ethanol and higher alcohols were observed as side products

(91) Iglesia, E. *Isobutanol-methanol mixtures from synthesis gas*; DE-AC22-94PC94066, Department of Energy: Washington, DC, September, 1998.
(92) Beretta, A.; Sun, Q.; Herman, R. G.; Klier, K. *Ind. Eng. Chem. Res.* **1996**, *35*, 1534.
(93) Beretta, A.; Lietti, L.; Tronconi, E.; Forzatti, P.; Pasquon, I. *Ind. Eng. Chem. Res.* **1996**, *35*, 2154.
(94) Epling, W.; Hoflund, G. B.; Minahan, D. M. *J. Catal.* **1998**, *175*, 175.
(95) Minahan, D. M.; Epling, W. S.; Hoflund, G. B. *Appl. Catal. A: General* **1998**, *166*, 375.
(96) Hoflund, G. B.; Epling, W. S.; Minahan, D. M. *Catal. Lett.* **1999**, *62*, 169.
(97) Epling, W. S.; Hoflund, G. B.; Minahan, D. M. *Appl. Catal. A: General* **1999**, *183*, 335.
(98) Jiang, T.; Niu, Y.; Zhong, B. *Fuel Process. Technol.* **2001**, *73*, 175.
(99) Chaumette, P.; Courty, Ph.; Kiennemann, A.; Kieffer, R.; Boujana, S.; Martin, G. A.; Dalmon, J. A.; Meriaudeau, P.; Mirodatos, C.; Holhein, B.; Mausbeck, D.; Hubert, A. J.; Germain, A.; Noel, A. *Ind. Eng. Chem. Res.* **1994**, *33*, 1460.

Table 5. Selected High-Temperature and Low-Temperature Methanol Synthesis Catalysts Employed in the Direct Conversion of Syngas to Ethanol and Mixed Alcohols

	experimental conditions					alc STY (mg/(g cat h))				
catalyst	temp (°C)	press (psig)	GHSV (h^{-1})	H_2/CO	X_{CO}[a] (%)	C_1-OH	C_2-OH	$\Sigma_{alcohol}$	Σ_{HC}. STY (mg/(g cat h)	ref
K_2O–Pd–ZrO_2–ZnO–MnO[b]	400	3626	99000	1.0	NA	1331	320	2012	NA	48
4 mol %Cs–ZnO–Cr_2O_3	405	1100	18000	0.75	4.5	173.4	2.7	288.1	19.7	92
3 wt % Cs–5.9 wt % Pd–ZnO–Cr_2O_3	440	1500	NA	1.0	19.0	60.0	5.0	196.0	228.0	94
3 wt % K–5.9 wt % Pd–ZnO–Cr_2O_3	440	1500	NA	1.0	14	54.0	8.0	221.0	111.0	97
3 mol % Cs–Cu–ZnO–Cr_2O_3	325	1100	5450	0.75	19.7	268.0	20.0	433.2	24.0	92
3 mol % Cs–Cu–ZnO–Cr_2O_3	325	1100	12000	0.75	13.8	844.5	59.1	1193.3	21.3	92
3 mol % Cs–Cu–ZnO–Cr_2O_3	325	1100	18000	0.75	11.7	1200	68.7	1547.1	18.5	92
4 mol % Cs–Cu–ZnO–Cr_2O_3	275	1100	3200	0.45	NA	271	24.6	322.6	NA	102
3 mol % Cs–Cu–ZnO–Cr_2O_3	310	1100	5450	0.45	20.2	231	22.3	334.7	15.8	92

[a] X_{CO} = CO conversion; C_1-OH = methanol; C_2-OH = ethanol; alc STY = space time yield of alcohol; $\Sigma_{alcohol}$ = sum of all the alcohols; NA = data not available. [b] Data was obtained using a continuous stirred-tank reactor (CSTR), while other data were obtained using fixed-bed reactors.

in methanol synthesis using these catalysts, especially when the catalysts were prepared by coprecipitation using alkali such as Na_2CO_3 and NaOH, because traces of alkali metal remained as an impurity in the catalyst.[100] The yield and selectivity of higher alcohols were found to increase with increasing alkali content. This observation prompted the development of alkali-modified ZnO/Cr_2O_3 and Cu/ZnO-based methanol synthesis catalysts for the synthesis of higher alcohols. Various alkali promoters such as Li, Na, K, and Cs with different alkali loading have been explored. The ZnO/Cr_2O_3 high-temperature methanol synthesis catalysts typically work at 350–450 °C and 120–300 atm (1700–4410 psig) and produced a mixture of methanol and isobutanol as major alcohol products with a small amount of ethanol.[38,46–48,92–98] The rate of isobutanol productivity increased with increasing alkali (K or Cs) loading.[95] The addition of a small amount of Pd to the ZnO/Cr_2O_3 formulation further improved the isobutanol selectivity.[46–48,96,97,99] However, high-temperature operation produces large quantities of hydrocarbons together with alcohol products.

Alkali-promoted Cu/ZnO-based methanol synthesis catalysts have been extensively studied for the synthesis of higher alcohols in the temperature range between 275 and 310 °C and pressure range between 750 and 1500 psig.[38,46–48,100–112] Most of these catalysts used either Al_2O_3 or Cr_2O_3 as a support and were prepared by coprecipitation techniques followed by impregnation of promoters such as K or Cs. The catalysts produced a mixture of linear and branched alcohols ranging from C_1–C_6 together with a small amount of other oxygenates and hydrocarbons. As stated above, most of these studies have focused on the synthesis of a mixture of methanol and higher alcohols. The STY of ethanol in these studies varied between 20 and 70 mg/(g cat h) depending upon the type of catalyst used and reaction operating conditions employed. (Table 5). Other supports such as MgO–CeO_2 have also been employed, probably to increase the basicity of the catalyst and hence to enhance the aldol-type condensation of lower alcohols to higher alcohols, especially to isobutanol.[103–105] As discussed in section 2.0, the Cu/ZnO–Al_2O_3 catalyst supplied by Sud-Chemie for the Lurgi–Octamix process produced methanol as the major oxygenated product.[46–48] The average carbon number of the oxygenated products was lower compared to that obtained over ZnO/Cr_2O_3 catalysts.[47] The presence of MnO in the catalyst formulation improved the ethanol production rate. Among various alkali metal promoters studied, Cs exhibited a better performance, and this could be due to higher basicity of the catalyst. Elevated levels of CO_2 in the syngas inhibit the synthesis of higher alcohols.

Kulawska and Skrzypek[109] have investigated the kinetics of syngas conversion to higher alcohols over a Cs-doped CuO–ZnO catalyst. At 350 °C, 1450 psig, and 7000 h^{-1} GHSV, the catalyst exhibited below 1% CO conversion, with an ethanol yield of about 26 mg/(g cat h). The ethanol selectivity was approximately 15%.

Xu et al.[110,111] have reported Fe-modified $CuMnZrO_2$ catalysts for the synthesis of higher alcohols. The $CuMnZrO_2$ catalyst was synthesized by coprecipitation. A small amount of Fe with a Cu:Mn:Zr:Fe molar ratio of 1:0.5:2:0.1 was added either by impregnation or by coprecipitation along with CuMn and Zr. Reaction of syngas ($H_2/CO = 2$) at 310 °C and about 900 psig pressure exhibited a CO conversion of about 45% with about 26% carbon selectivity for total alcohols, including methanol. Among the C_{2+} higher alcohols, ethanol was the highest, and its distribution increased from about 12 to about 15% with increasing CO conversion from about 25 to 50%.

b. Modified Fischer–Tropsch Synthesis Catalysts. Traditional Fischer–Tropsch (FT) synthesis catalysts contain Co, Fe, Ni, or Ru metal supported on SiO_2 or Al_2O_3 with promoters such as Cu, K, etc.[113,114] These catalysts produce long-chain hydrocarbons with a small amount of oxygenates, including alcohols. The yield and selectivity of oxygenates could be significantly improved by suitably modifying FT synthesis catalysts by promoting with transition metals and alkali cations.[115–137] Consequently, a wide range of metal promoters, such as Cu, Mo, Mn, Re, Ru, etc., and alkali promoters, such as Li, K, Cs, Sr, etc., have been added to Co or Fe catalysts supported on SiO_2 or Al_2O_3. The nature of the metal promoter and its precursor, and loading, and the type of alkali cation used all play a significant role in controlling the yield and selectivity toward alcohols. For Co-based catalysts, it appears that catalysts prepared by using either $Co(CO)_8$ or cobalt acetate exhibit better

(100) Smith, K. J.; Anderson, R. B. *Can. J. Chem. Eng.* **1983**, *61*, 40.
(101) Calverley, E. M.; Smith, K. *J. Catal.* **1991**, *130*, 616.
(102) Campos-Martin, J. M.; Fierro, J. L. G.; Guerreri-Ruiz, A.; Herman, R. G.; Klier, K. *J. Catal.* **1996**, *163*, 418.
(103) Apesteguia, C. R.; De Rites, B.; Miseo, S.; Soled, S. *Catal. Lett.* **1997**, *1*.
(104) Xu, M.; Gines, M. J. L.; Hilmen, A.; Stephens, B. L.; Iglesia, E. *J. Catal.* **1997**, *171*, 130.
(105) Xu, M.; Iglesia, *Catal. Lett.* **1998**, *51*, 47.
(106) Klier, K.; Beretta, A.; Sun, Q.; Feeley, O. C.; Herman, R. G. *Catal. Today* **1997**, *36*, 3.
(107) Burcham, M. M.; Herman, R. G.; Klier, K. *Ind. Eng. Chem. Res.* **1998**, *37*, 4657.
(108) Kulawska, M. *React. Kinet. Catal. Lett.* **1999**, *68*, 207.
(109) Kulawska, M.; Skrzypek, J. *Chem. Eng. Process* **2001**, *40*, 33.
(110) Xu, R.; Yang, C.; Wei, W.; Li, W.; Sun, Y.; Hu, T. *J. Mol. Catal. A: Chemical* **2004**, *221*, 51.
(111) Xu, R.; Wei, W.; Li, W.; Hu, T.; Sun, Y. *J. Mol. Catal. A: Chemical.* **2005**, *234*, 75.
(112) Nowicki, L. *Chem. Eng. Process* **2005**, *44*, 383.
(113) Davis, B. H. *Top. Catal.* **2005**, *32*, 143.
(114) Dry, M. E. *J. Chem. Tech. Biotech.* **2002**, *77*, 43.

Table 6. Selected Modified Fischer–Tropsch Catalysts Employed in the Direct Conversion of Syngas to Ethanol and Mixed Alcohols

	experimental conditions					carbon selectivity (%)[b]					alc STY (mg/(g cat h))		
catalyst	temp (°C)	press (psig)	GHSV (h^{-1})	H_2/CO	X_{CO}[a] (%)	HC[c]	CO_2	C_1-OH	C_2-OH	C_{3+}-OH	EtOH	$\Sigma_{alcohol}$	ref
Co–Re–Sr/SiO_2 [d]	250	300	2000	2.0	4.9	63.0	Tr	4.7	22.0	3.7	NA	NA	119
Fe/Al_2O_3	200	116	40,000	2.0	<1.0	35.0	NA	42	20.0	3.0	NA	NA	118
Co–Re–Sr/SiO_2 [d]	250	305	2000	2.0	5.0	18.0	6.0	2.8	20.4	NA	NA	NA	123
Co–Ru–Sr/SiO_2 [d]	250	305	2000	2.0	4.5	50.0	7.0	4.4	22.5	NA	NA	NA	123
Co–Ir–Sr/SiO_2 [d]	220	305	2000	2.0	2.2	34.0	0.0	8.7	37.0	NA	NA	NA	123
$KLaCo_{0.7}Cu_{0.3}O_{3-\delta}$	275	1000	5000	2.0	NA	51.1	NA	11.4	16.2	21.3	NA	~37	137

[a] X_{CO} = CO conversion; HC = total hydrocarbons including methane; C_1-OH = methanol; C_2-OH = ethanol; C_{3+}-OH = all the alcohol products except methanol and ethanol; alc STY = space time yield of alcohol; $\Sigma_{alcohol}$ = sum of all the alcohols. [b] Carbon selectivity is defined as the selectivity of all the carbon-containing products formed from converted carbon, and the values are recalculated from the original reported data. They may be CO_2-free if CO_2 data are not available (NA). [c] HC = hydrocarbon selectivity calculated from the alcohol selectivity data. This may include CO_2 selectivity: NA = data not available; Tr = trace quantity. [d] Other products include C_2-oxygenates.

performance due to an improved Co dispersion achieved by using these precursors upon decomposition. Most of these catalytic systems produce hydrocarbons including methane as the predominant product with a hydrocarbon/alcohol selectivity of 1 or even higher. The alcohol products formed over modified FT synthesis catalysts are generally straight-chain primary alcohols. The distribution of hydrocarbons and alcohol products follow an Anderson–Schulz–Flory (ASF) distribution. A few selected catalysts for the conversion of syngas to ethanol and mixed alcohols are summarized in Table 6.

Tukeuchi et al.[119] have reported Co/SiO_2 catalysts modified with Re and Sr for the synthesis of ethanol from syngas. Addition of Re enhanced the catalytic activity, while Sr improved the selectivity toward ethanol by suppressing the formation of hydrocarbons. They have reported that a maximum ethanol selectivity could be obtained over Co/SiO_2 catalyst modified with about 4 wt % Re and 4 wt % Sr. The amount of C_2-oxygenates formed was higher than that expected from an ASF distribution, while the sum of hydrocarbon and C_2-oxygenates followed the ASF distribution.

Matsuzaki et al.[120] have also reported the effect of various transition metals on the formation of oxygenates from syngas over Co/SiO_2 catalysts. The catalysts have been modified by a wide range of transition metals such as Re, Ru, Ir, Rh, Os, Pt, Pd, Au, Ag, Cu, Mo, Mn, Cr, etc. using different metal precursors for each metal. A high selectivity to ethanol has been observed when the precursors for both Co and the promoter transition metal are from carbonyls or acetates. On the basis of extensive catalyst characterizations, the authors noted that highly dispersed Co metal is the main active site on these catalysts and that transition metals promote the reduction of the Co^{2+} cation to a metallic state by a hydrogen spillover mechanism.

IFP filed a number patents on the development of CuCo-based modified FT synthesis catalysts for the synthesis of higher alcohols.[54,138–144] These catalysts are a complex mixture containing three or more metals from the group Cu, Co, and Al or Cr, Zn, V, Mn, Yb, Zr, Th, etc. and an alkali metal such as K, Cs, Ca, Ba, La, etc. An important prerequisite for a better catalytic performance is the homogeneity of the catalyst precursors during preparation. These catalysts are generally prepared by a coprecipitation method followed by impregnation of a small amount of alkali promoters. Typical operating conditions for these catalysts are 50–150 bar (725–2175 psig), 220–350 °C, 4000–8000 GHSV using a wide range of H_2/CO ratio. In most of the cases, the feed mixture contained a significant amount (≈19%) of CO_2. The patents also suggest that catalyst activation processes, via reduction by continuously flowing H_2, are necessary to increase the catalytic activity.

The performance of a few selected catalysts from IFP patents are summarized in Table 7. It can be seen that the CuCo-based catalysts modified by Cr, Mn, Fe, La, and K are active and produce relatively high yields of ethanol ranging from 100 to 300 mg/(g cat h). These are 3–6 times higher than those observed over some of the modified methanol synthesis catalysts (see Table 5). The ethanol yield over CuCo-based catalysts reported in the IFP patents is higher than that of methanol or a mixture of methanol and C_{3+}-alcohols, indicating that these catalysts systems are relatively more selective for ethanol. The C_{3+}-alcohols formed include both linear and branched alcohols with high yields toward linear alcohols. However, a large amount of CH_4 and higher hydrocarbons could also be formed over these catalysts. Unfortunately, the yield and selectivity of hydrocarbons and CO_2 are rarely reported in these patents.

Following this early work from IFP, a wide range of CuCo-based higher alcohol synthesis catalysts have been reported in

(115) Inoue, M.; Miyake, T.; Takegami, Y.; Inui, T. *Appl. Catal.* **1984**, *11*, 103.
(116) Razzaghi, A.; Hindermann, J.; Kiennemann, A. *Appl. Catal.* **1984**, *13*, 193.
(117) Fujimoto, K.; Oba, T. *Appl. Catal.* **1985**, *13*, 289.
(118) Pijolat, M.; Perrichon, V. *Appl. Catal.* **1985**, *13*, 321.
(119) Naidu, S.; Siriwardane, U. *Novel preparation and magneto chemical characterization of nano-particle mixed alcohol catalysts*; DOE Grant No. DE-FG2626-00NT40836, Department of Energy: Washington, DC, August 2003.
(120) Takeuchi, K.; Matsuzaki, T.; Hanaoka, T.; Wei, K. *J. Mol. Catal.* **1989**, *55*, 361.
(121) Xiaoding, X.; Mausbeck, D.; Scholten, J. J. F. *Catal. Today* **1991**, *10*, 429.
(122) Pereira, E. B.; Martin, G. *Appl. Catal. A: General* **1993**, *103*, 291.
(123) Bhasin, M. M.; Bartley, W. J.; Ellgen, P. C.; Wilson, T. P. *J. Catal.* **1978**, *54*, 120.
(124) Wilson, T. P.; Kasai, P. H.; Ellen, P. C. *J. Catal.* **1981**, *69*, 193.
(125) Mouaddib, N.; Perrichon, V.; Martin, G. A. *Appl. Catal. A: General* **1994**, *118*, 63.
(126) Chu, W.; Kieffer, R.; Kiennemann, A.; Hindermann, J. P. *Appl. Catal. A: General* **1995**, *121*, 95.
(127) Fraga, M. A.; Jordao, E. *React. Kinet. Catal. Lett.* **1998**, *64*, 331.
(128) Llorca, Homs, N.; Rossell, O.; Seco, M.; Fierro, J. L.; Piscina, P. R. *J. Mol. Catal. A: Chemical* **1999**, *149*, 225.
(129) Volkova, G. G.; Yurieva, T. M.; Plyasova, L. M.; Naumova, M. I.; Zaikovskii, V. I. *J. Mol. Catal. A: Chemical* **2000**, *158*, 389.
(130) Aquino, A.; Cobo, A. *Catal. Today* **2001**, *65*, 209.
(131) Boz, I. *Catal. Lett.* **2003**, *87*, 187.
(132) de la Pena O'Shea, V. A.; Menendez, N. N.; Tornero, J. D.; Fierro, J. L. G. *Catal. Lett.* **2003**, *88*, 123.
(133) Zhang, H.; Dong, X.; Lin, G.; Liang, X.; Li, H. *Chem. Commun.* **2005**, 5094.
(134) Mahdavi, V.; Peyrovi, M. H.; Islami, M.; Mehr, Y. *Appl. Catal. A: General* **2005**, *281*, 259.
(135) Tien-Thao, N.; Alamdari, H.; Zahedi-Niaki, M. H.; Kaliaguine, S. *Appl. Catal. A: General* **2006**, *311*, 204.
(136) Mahdavi, V.; Peyrovi, M. H. *Catal. Commun.* **2006**, *7*, 542.
(137) Tien-Thao, N.; Zahedi-Niaki, M. H.; Alamdari, H.; Kaliaguine, S. *J. Catal.* **2007**, *245*, 348.
(138) Sugier, A.; Freund, E. *Process for manufacturing alcohols, particularly linear saturated primary alcohols, from synthesis gas*. U.S-.Patent No. 4122110, October 1978.

Table 7. Selected CuCo-Based Catalysts Patented by IFP for the Direct Conversion of Syngas to Ethanol and Mixed Alcohols

	experimental conditions					alc STY (mg/(g cat h))				
catalyst	temp (°C)	press (psig)	GHSV (h^{-1})	$H_2/(CO + CO_2)$	X_{CO}[a] (%)	C_1-OH	C_2-OH	$\Sigma_{alcohol}$	Σ_{HC}. STY (mg/(g cat h))	ref
$Cu_{1.0}Co_{1.0}Cr_{0.8}K_{0.09}$ + cement	250	870	4000	2.0	NA	76	125	316	NA	138
$Cu_{1.0}Co_{1.0}Cr_{0.8}K_{0.09}$ + cement	250	1740	4000	2.0	NA	130	244	640	NA	138
$Cu_{1.0}Co_{1.0}Cr_{0.8}K_{0.09}$ + cement	250	1740	8000	2.0	NA	208	341	729	NA	138
$Cu_{1.0}Co_{0.7}Zn_{0.3}Cr_{0.8}K_{0.09}$	250	870	4000	2.0	NA	81	119	250	NA	139
$Cu_{1.0}Co_{1.0}Cr_{0.5}La_{0.3}K_{0.09}$	250	870	4000	2.0	NA	87	149	376	NA	139
$Cu_{1.0}Co_{1.0}Mn_{0.8}K_{0.12}$	250	870	4000	2.0	NA	79	135	327	NA	139
$Cu_{1.0}Co_{1.0}Fe_{0.8}K_{0.12}$	250	870	4000	2.0	NA	62	128	296	NA	139

[a] X_{CO} = CO conversion; C_1-OH = methanol; C_2-OH = ethanol; alc STY = space time yield of alcohol; $\Sigma_{alcohol}$ = sum of all the alcohols; NA = data not available.

the open literature.[125,126,128,129,131–137] Similar to the IFP catalysts, the CuCo-based catalysts reported in the literature also produced mainly primary alcohols. The selectivity for alcohols depends on the type of metal and alkali ion promoters used. On the basis of catalyst characterization data, researchers linked the yield and selectivity of higher alcohols to physicochemical properties of the catalysts such as metal particle sizes, dispersions, and redox properties. The interaction between highly dispersed Co and Cu metallic particles, or in other words, a Cu–Co synergistic interaction in these catalyst systems, is important in catalytic activity for higher alcohols synthesis.[128,145,146]

Tien-Thao, et al.[135,137] have recently reported $LaCo_{1-x}Cu_xO_{3-\delta}$ perovskite catalysts for the conversion of syngas to higher alcohols at 275 °C and 1000 psig pressure. The catalysts produced a mixture of C_1–C_7 alcohols containing 5–10% ethanol together with a large amount (about 50%) of hydrocarbons. Alkali promotion improved the ethanol selectivity further. Among the various alkali promoters tested, K was found to be better and exhibited a relatively higher selectivity for ethanol. The study noted that copper located outside of the perovskite lattice was responsible for the formation of methanol and methane while those located in the octahedral position of the perovskite lattice favored alcohol formation.

c. Unsulfided Molybdenum-Based Catalysts. Unsulfided Mo-based catalysts promoted by base metals, alkali, and noble metals have been reported by a number of researchers for the conversion of syngas to alcohols.[147–153] As usual, all these reports focused on the synthesis of mixed alcohols, and no data on the yield and selectivity of ethanol were reported. On the other hand, Li et al.[155] have reported the formation of 10–15% ethanol over K-promoted Mo catalyst supported on activated carbon (Mo–K/C). Zhang et al.[156] have studied HAS over catalysts of varying Co to Mo ratios while keeping the K loading to about 1 wt %. Experiments were carried out at 300 °C and 900 psig pressure at a space velocity of 10 000 h^{-1} with a syngas containing an H_2/CO ratio of 2. The best catalyst at a Co to Mo ratio of 1 to 7 gave a total alcohol productivity of 624 g/(kg cat h), which is close to that reported for some of the CuCo-based IFP catalysts (see Table 7). Under these conditions, the total alcohol selectivity was about 48%. The single-pass CO conversion was 37.5%, with an ethanol selectivity of about 25%.

Recently, K-promoted Co or Ni-doped β-Mo_2/C catalysts have been reported for the conversion of syngas to higher alcohols.[157,158]The undoped and unmodified β-Mo_2/C exhibited a CO conversion of about 58% but produced CO_2 and hydrocarbons as major products. The addition of K decreased the CO conversion to about 23% and increased the selectivity to alcohols, with an ethanol distribution of about 40% among the alcohol products formed. Both the alcohol selectivity and CO conversion increased upon doping Ni onto K-modified β-Mo_2C. Thus, the K-Ni-βMo_2/C catalyst under the above experimental conditions exhibited a high CO conversion of about 73%, with an alcohol selectivity of about 23%. The alcohol mixture contained about 40% ethanol. Conversely, doping of Co instead of Ni increased the selectivity of hydrocarbons without influencing the selectivity to alcohols. Both Ni and Co have been reported to exert a promotional effect for the carbon-chain growth, especially for the conversion of C_1 to C_2 species. The presence of both Co_3Mo_3C and Co_2C phases have been identified in the Co-doped catalysts. The presence of the Co_2C phase has been reported to favor the formation of hydrocarbons. The catalytic performance data of some of these catalysts are gathered in Table 8. The C_{3+} higher alcohols in these catalysts are mainly linear alcohols.

d. Sulfided Molybdenum-Based Catalysts. Sulfided Mo-based

(139) Sugier, A.; Freund, E. *Process for manufacturing alcohols and more particularly saturated linear primary alcohols from synthesis gas*. U.S. Patent No. 4,291,126, September 1981.
(140) Sugier, A.; Freund, E.; Page, J. L. *Production of alcohols from synthesis gases*. U.S. Patent No. 4,346,179, August 1982.
(141) Courty, P.; Durand, D.; Sugier, A.; Edouard, F. *Process for manufacturing a mixture of methanol and higher alcohols from synthesis gas*. U.S.Patent No. 4,659,742, April 1987.
(142) Courty, P.; Durand, D.; Forestiere, A.; Grandvallet, P. E. *Process of use of a catalyst for synthesizing saturated primary aliphatic alcohols*. U.S. Patent No. 4,675,343, June 1987.
(143) Chaumette, P.; Courty, P.; Durand, D.; Grandvallet, P.; Travers, C. *Process for synthesizing a mixture of primary alcohols from a synthesis gas in the presence of a catalyst containing copper, cobalt, zinc, and aluminum*. U.S. Patent No. 4,791,141, December 1988.
(144) Courty, P.; Chaumette, P.; Durand, D.; Verdon, C. *Process for manufacturing of primary alcohols from a synthesis gas in the presence of a catalyst containing copper, cobalt, zinc, and at least one alkali and/or alkaline earth metal*. U.S. Patent No. 4,780,481, October 1988.
(145) Velu, S.; Suzuki, K.; Hashimoto, S.; Satoh, N.; Ohashi, F.; Tomura, S. *J. Mater. Chem.* **2001**, *11*, 2049.
(146) Di Cosimo, J. I.; Marchi, A. J.; Apesteguía, C. R. *J. Catal.* **1992**, *134*, 594.
(147) Inoue, M.; Miyake, T.; Takegami, Y.; Inui, T. *Appl. Catal.* **1987**, *29*, 285.
(148) Inoue, M.; Miyake, T.; Yonezawa, S.; Medhanavyn, D.; Takegami, Y.; Inui, T. *J. Mol. Catal.* **1998**, *45*, 111.
(149) Inoue, M.; Kurusu, A.; Wakamatsu, H.; Nakajima, K.; Inui, T. *Appl. Catal.* **1987**, *29*, 374.
(150) Inoue, M.; Nakajima, K.; Kurusu, A.; Miyake, T. *Appl.Catal.* **1989**, *49*, 213.
(151) Alyea, E. C.; He, D.; Wang, J. *Appl. Catal. A: General* **1993**, *104*, 77.
(152) Avila, Y.; Kappenstein, C.; Pronier, S.; Barrault, J. *Appl. Catal. A: General* **1995**, *132*, 97.
(153) Storm, D. A. *Top. Catal.* **1995**, *2*, 91.
(154) Li, X.; Feng, L.; Zhang, L.; Dadyburjor, D. B.; Kugler, E. L. *Molecules* **2003**, *8*, 13.
(155) Li, X.; Feng, L.; Zhenyu, L.; Zhong, B.; Dadyburjor, D. B.; Kugler, E. L. *Ind. Eng. Chem. Res.* **1998**, *37*, 3863.
(156) Zhang, Y.; Sun, Y.; Zhong, B. *Catal. Lett.* **2001**, *76*, 249.
(157) Xiang, M.; Li, D.; Li, W.; Zhong, B.; Sun, Y. *Catal. Commun.* **2007**, *8*, 503.
(158) Xiang, M.; Li, D.; Li, W.; Zhong, B.; Sun, Y. *Catal. Commun.* **2007**, *8*, 513.

Table 8. Selected Unsulfided Mo-Based Catalysts Reported for the Direct Conversion of Syngas to Ethanol and Mixed Alcohols

	experimental conditions					carbon selectivity (%)[b]					alc STY (mg/(g cat h))		
catalyst	temp (°C)	press (psig)	GHSV (h^{-1})	H_2/CO	X_{CO}[a] (%)	HC	CO_2	C_1-OH	C_2-OH	C_{3+}-OH	EtOH	$\Sigma_{alcohol}$	ref
1%K–Co_1Mo_4ultrafine	300	870	10000	2.0	27.5	56.9[c]	NA	21.6	13.1	8.4	NA	390.5	156
1%K–Co_1Mo_4ultrafine	300	870	10000	2.0	37.5	51.5[c]	NA	23.4	12.1	13.0	NA	624.4	156
1%K–Co_1Mo_{10} ultrafine	300	870	10000	2.0	23.7	59.7[c]	NA	20.7	12.7	6.9	NA	267.0	156
K–β-Mo2C[d]	300	1160	2000	1.0	23.4	23.9	49.6	9.5	11.1	5.7	NA	NA	158
K–Ni–β-Mo_2C[d]	300	1160	2000	1.0	73.0	25.8	50.9	6.0	9.4	7.2	NA	NA	158
K–Co–β-Mo_2C-10[d,e]	300	1160	2000	1.0	36.7	61.4	NA	11.3	13.9	24.0	NA	134.4	157
K–Co–β-Mo_2C-4[d,f]	300	1160	2000	1.0	62.9	70.2	NA	8.6	11.5	9.7	NA	145.7	157

[a] X_{CO} = CO conversion; HC = total hydrocarbons including methane; C_1-OH = methanol; C_2-OH = ethanol; C_{3+}-OH = all the alcohol products except methanol and ethanol; alc STY = space time yield of alcohol; $\Sigma_{alcohol}$ = sum of all the alcohols; other products include C_2-oxygenates; NA = data not available; Tr = trace quantity. [b] Carbon selectivity is defined as the selectivity of all the carbon-containing products formed from converted carbon, and the values are recalculated from the original reported data. They are CO_2-free except for $K_2CO_3CoSMoS_2$. [c] HC = hydrocarbon selectivity calculated from the alcohol selectivity data. This may include CO_2 selectivity. [d] Catalyst contained K/Mo = 0.2 and used K_2CO_3 as the K precursor. [e] Mo/Co = 10. [f] Mo/Co = 4.

Table 9. Selected MoS_2-Based Catalysts Reported for the Direct Conversion of Syngas to Ethanol and Mixed Alcohols

	experimental conditions					carbon selectivity (%)[b]					alc STY (mg/(g cat h))		
catalyst	temp (°C)	press (psig)	GHSV (h^{-1})	H_2/CO	X_{CO}[a] (%)	HC	CO_2	C_1-OH	C_2-OH	C_{3+}-OH	EtOH	$\Sigma_{alcohol}$	ref
MoS_2 (Dow Chemical)	295	1050	1300	1.0	29.2	14.5	NA	22.7	40.7	17.4	NA	NA	163
$KRhMoS_2/Al_2O_3$	327	1450	4800	2.0	11.1	41.0[c]	NA	11.0	19.0	29.0	NA	174[d]	169
$KRhMoS_2/Al_2O_3$	327	1450	14400	2.0	5.5	17.0[c]	NA	26.0	28.0	28.0	NA	389[d]	169
$KCoMoS_2$/C-1[f]	330	725	4800	2.0	14.5	72.6[d]	NA	11.1	10.6	5.6	NA	108[d]	170
$KCoMoS_2$/C-4[g]	330	725	4800	2.0	11.7	58.1[d]	NA	18.7	13.2	8.0	NA	150[d]	170
$KCoMoS_2$/C-16[h]	330	725	4800	2.0	8.7	60.7c	NA	19.6	16.1	5.6	NA	96[d]	170
$K_2CO_3CoMoS_2$	270	2100	2546	1.1	10.4	12.7	1.70	48.2	29.6	7.8	NA	250	172
$LaKNiMoS_2$	320	1160	2500	1.0	33.5	34.0c	NA	7.5	18.5	40.0	NA	170[d]	176
$K_2CO_3NiMoS_2$	320	1160	2500	1.0	55.6	52.6	NA	6.2	15.4	25.8	NA	153[e]	177
$K_2CO_3NiMoS_2$	280	1160	2500	1.0	20.6	36.6	NA	10.8	27.2	25.4	NA	102	177
$Cs_2CO_3CoMoS_2$/clay	320	2000	4000	1.1	28.7	31.3	NA	10.8	30.3	22.0	NA	NA	179
$K_2CO_3CoMoS_2$/clay	320	2000	4000	1.1	31.9	36.0	NA	13.5	23.1	21.6	NA	NA	179

[a] X_{CO} = CO conversion; HC = total hydrocarbons including methane; C_1-OH = methanol; C_2-OH = ethanol; C_{3+}-OH = all the alcohol products except methanol and ethanol; alc STY = space time yield of alcohol; $\Sigma_{alcohol}$ = sum of all the alcohols; NA = data not available. [b] Carbon selectivity is defined as the selectivity of all the carbon-containing products formed from converted carbon, and the values are recalculated from the original reported data and they are CO_2-free except for $K_2CO_3CoSMoS_2$. [c] HC = hydrocarbon selectivity calculated from the alcohol selectivity data. This may include CO_2 selectivity. [d] Space time yield (mL/(L cat h)). [e] Space time yield (kg/(mL cat h)). [f] The Mo/Co = 1. [g] The Mo/Co = 4. [h] The Mo/Co = 16.

catalysts are well-known in petroleum industries as hydrodesulfurization and hydrodenitrogenation catalysts.[159,160] In addition, these catalysts have also been evaluated for HAS from syngas.[31,38,50,53] Although undoped MoS_2 produced only hydrocarbons, primarily methane, the selectivity dramatically shifted toward alcohols upon alkali promotion. The Dow Chemical Company[56,161] and the Union Carbide Corporation[162] independently demonstrated that either supported or unsupported alkali-doped MoS_2 catalyst could produce alcohols from syngas, with alcohol selectivity ranging from 75 to 90%.[163,164] It has been claimed that, by manipulating the composition of catalysts and reaction operating conditions, it is possible to vary the ratio of methanol to C_{2+} alcohols within wide limits. The role of alkali promoters in these catalysts is to shift the products from hydrocarbons to alcohols.

Following these early reports, several researchers have investigated the Mo_2S-based catalysts for HAS.[165–181] The selectivity between hydrocarbons and total alcohols varied depending upon the type of promoter used and the reaction operating conditions employed. Table 9 presents the performance of a few MoS_2-based catalyst compositions reported for the conversion of syngas to mixed alcohols. A high selectivity to ethanol around 40% (CO_2-free basis) has been claimed in the Dow patent[163] while others have obtained an ethanol selectivity ranging from 10 to 30% (see Table 9) depending upon the type of catalyst used and reaction operating conditions employed. The C_{3+} higher alcohols formed over these catalysts are generally linear alcohols. A total alcohol yield of 100–400 mg/(g cat h) obtained over these catalysts is lower than that

(159) Chianelli, R. R. *Catal. Rev. Sci. Eng.* **1984**, *26*, 361.
(160) Curtis, C. W.; Cahela, D. R. *Energy Fuels* **1989**, *3*, 168.
(161) Quarderer, Q. J.; Cochram, G. A. *Catalytic process for producing mixed alcohols from hydrogen and carbon monoxide*. PCT Int. Pat. Publication No. WO84/03696, September 1984.
(162) Kinkade, N. E. *Process for producing alcohols from carbon monoxide and hydrogen using an alkali-molybdenum sulfide catalyst*. PCT Int. Pat. Publication No. WO 85/03073, July 1985.
(163) Stevens, R. R. *Process for producing alcohols from synthesis gas*. U.S. Patent No. 4,882,360, November 1989.
(164) Kinkade, N. E. *Tantalum-containing catalyst useful for producing alcohols from synthesis gas*. U.S. Patent No. 4,994,498, February 1991.
(165) Gang, L.; Chengfang, Z.; Yanqing, C.; Zhibin, Z.; Yianhui, N.; Linjun, C.; Fong, Y. *Appl. Catal. A: General* **1997**, *150*, 243.
(166) Park, T. Y.; Nam, I.; Kim, Y. G. *Ind. Eng. Chem. Res.* **1997**, *36*, 5246.
(167) Bian, G.; Fan, L.; Fu, Y.; Fujimoto, K. *Appl. Catal. A: General* **1998**, *170*, 255.
(168) Bian, G.; Fan, Li.; Fu, Y.; Fujimoto, K. *Ind. Eng. Chem. Res.* **1998**, *3*, 1736.
(169) Li, Z.; Fu, Y.; Jiang, M. *Appl. Catal. A: General* **1999**, *187*, 187.
(170) Li, Z.; Fu, Y.; Bao, J.; Jiang, M.; Hu, T.; Liu, T.; Xie, Y. *Appl. Catal. A: General* **2001**, *220*, 21.
(171) Li, Z.; Fu, Y.; Jiang, M.; Hu, T.; Liu, T.; Xie, Y. *J. Catal.* **2001**, *199*, 155.
(172) Iranmahboob, J.; Hill, D. O. *Catal. Lett.* **2002**, *78*, 49.
(177) Li, D.; Yang, C.; Li, W.; Sun, Y.; Zhong, B. *Top. Catal.* **2005**, *32*, 233.
(178) Li, D.; Yang, C.; Zhao, N.; Qi, H.; Li, W.; Sun, Y.; Zhong, B. *Fuel Process. Technol.* **2007**, *88*, 125.
(179) Iranmahboob, J.; Toghiani, H.; Hill, D. O. *Appl. Catal. A: General* **2003**, *247*, 207.
(180) Bao, J.; Fu, Y.; Sun, Z.; Gao., *Chem. Commun.* **2003**, 746.
(181) Koizumi, N.; Murai, K.; Ozaki, T.; Yamada, M. *Catal. Today* **2004**, *89*, 465.

reported by IFP of unsulfided Mo-based catalysts (140–650 mg/(g cat h); Table 8) and for CuC-based catalysts (300–750 mg/(g cat h); Table 7).

Li et al. [169]have reported a series of Rh-modified MoS_2-based catalysts containing 0–1 wt % Rh. The catalytic activity for alcohol synthesis increased with increasing Rh loading. On the basis of catalyst characterization data, the authors report that the addition of Rh improves the Mo dispersion. The interaction of Rh with Mo species may cause the basal planes of the MoS_2-like species to become oriented perpendicular to the support surface due to the favorable bonding between the MoS_2 edge planes and the support. The interaction between Rh and Mo species stabilizes the cationic and metallic Rh species, which favors the formation of C_{2+} higher alcohols. The same authors have also evaluated MoS_2-based catalysts supported on activated carbon and promoted by Co.[170] They observed that addition of Co to the K–MoS_2/C catalyst improves the yield of total alcohols. The selectivity of ethanol and higher alcohols also improved to some extent with increasing Co content. Higher yields of alcohols and selectivity toward ethanol have been observed for a catalyst containing a Co/Mo ratio of 0.5.

Iranmahboob and co-workers[172,179] have reported Co-modified MoS_2-based catalysts supported on activated carbon and clay for the conversion of syngas to higher alcohols. They observed a higher selectivity toward ethanol over these catalysts. The catalyst characterization data revealed the existence of Co_3S_4 and Co_9S_8 phases in their catalysts. The quantity of the later phase was found to increase with catalyst aging and this deactivated the catalyst. The formation of the later phase was found to be higher in Cs-promoted catalysts compared to their K-promoted counterparts. Consequently, the K-promoted catalyst was reported to be more active and selective for higher alcohols synthesis than Cs-promoted catalysts. The authors have claimed a higher ethanol yield of about 130 mg/(g cat h) over K-promoted Co–MS_2 supported on clay.[179]

Li and co-workers[176,177] have reported Ni-promoted K_2CO_3-modified MoS_2 catalysts for the conversion of syngas to mixed alcohols. The authors noted that addition of Ni to the K_2CO_3-modified MoS_2 catalyst decreases alcohol selectivity with concomitant increase in hydrocarbon selectivity. This is expected, taking into account the fact that Ni is a well-known methanation catalyst.[182] However, addition of Ni decreases the methanol selectivity and increases the selectivity toward C_{2+} higher alcohols, especially for ethanol. On the basis of kinetic studies, the authors noted that addition of Ni decreases the apparent activation energies of alcohols, especially for C_1–C_3 alcohols, while the apparent activation energy for butanol increases. The promotional activity of Ni in these catalytic systems has been attributed to the bifunctionality of Ni, namely, catalyzing the formation of alcohol precursor and subsequent CO insertion reactions. The hydrocarbon formation due to Ni addition could be suppressed by modifying the catalyst with La. Thus, the La-promoted Ni–K_2CO_3–MoS_2 catalyst exhibits a high selectivity of about 66% (CO_2-free basis) for alcohols with an ethanol selectivity of about 18%. The promotional effect of La has been attributed to a strong interaction between Ni and La, which helps improve the Ni dispersion on the surface of the catalyst.

MoS_2-based catalysts appear to be one of the most promising catalyst candidates at present for the conversion of syngas to ethanol and mixed alcohols. Some of the additional advantages of using these catalysts for practical applications include:

■ The MoS_2-based catalysts are sulfur-resistant and, in fact, require 50–100 ppm of sulfur in the form of H_2S in the syngas stream to maintain the sulfidity of the catalyst.[31,53,56] This reduces the risk of sulfur poisons and will probably reduce the cost of removing sulfur compounds from syngas streams.

■ Catalyst deactivation due to coke deposition is relatively less severe even with a syngas containing a low H_2/CO ratio of less than 2.

■ The catalyst favors the formation of linear alcohols, with a high relative selectivity to ethanol.

■ The catalysts are less sensitive to CO_2 in the syngas stream compared to other alcohol synthesis catalysts (this aspect is discussed below).

The traditional way to prepare MoS_2-based catalyst is by thermal decomposition or reduction of $(NH_4)_2MoS_4$. Development of novel technology for the synthesis of MoS_2-based catalysts with nanodispersion could improve the catalytic performance. As an example, Yoneyama and Song[183] have recently reported the synthesis of unsupported MoS_2-like catalyst by decomposing $(NH_4)_2MoS_4$ in an organic solvent such as *n*-tridecane with added water under H_2 pressure between 350 and 400 °C. The catalyst prepared by this route was found to be much more active in the hydrogenation of naphthalene compared to that prepared by the conventional method.

PowerEnerCat, Inc., has recently patented an improved nanosized MoS_2 catalyst for HAS by the Ecalene process.[56] The process uses a nanosized MoS_2 catalyst with a mean particle diameter of below 100 nm of Mo synthesized by a sonication method for the synthesis of mixed alcohols from syngas in a slurry reactor. The process, at approximately 280 °C and 2000 psig, produced mixed alcohols with a space time yield higher than 400 mg alcohol/(g cat h).

5.2.1.2.2. Role of Alkali Promoters. Alkali promoters such as Na, K, Cs, Sr, Ba, etc. have been widely employed in various catalytic systems including Fe-based Fischer–Tropsch synthesis catalysts and CuZn-based, ZnO–Cr_2O_3-based, and MoS_2-based higher alcohol synthesis catalysts as well as in alcohol and hydrocarbon reforming catalysts.[38,46–48,101,184–187] They play a significant role in activity, selectivity, and lifetime of the catalysts. Addition of these basic promoters could neutralize the surface acidity, thereby suppressing various unwanted side reactions such as isomerisation, dehydration and coke deposition, etc. In Fe-based FT synthesis catalysts, the added alkali (K in general) has been found to increase the rate of carbon chain growth and to increase the selectivity to olefins.[184]

In CO hydrogenation reactions, it is generally believed that the CO molecules adsorbed dissociatively are responsible for hydrocarbon formation while those adsorbed associatively favor the formation of alcohols.[46,188] In alcohol synthesis catalysts,

(173) Iranmahboob, J.; Toghiani, H.; Hill, D. O.; Nadim, F. *Fuel Process. Technol.* **2002**, *79*, 71.
(174) Iranmahboob, J.; Hill, D. O.; Toghiani, H. *Appl. Catal. A: General* **2002**, *231*, 99.
(175) Iranmahboob, J.; Toghiani, H.; Hill, D. O. *Appl. Catal. A: General* **2003**, *247*, 207.
(176) Li, D.; Yang, C.; Qi, H.; Zhang, H.; Li, W.; Sun, Y.; Zhong, B. *Catal. Commun.* **2004**, *5*, 605.
(182) Sehested, J.; Dahl, S.; Jacobsen, J.; Rostrup-Nielsen, J. R. *J. Phys. Chem. B* **2005**, *109*, 2432.
(183) Yoneyama, Y.; Song, C. *Catal. Today* **1999**, *50*, 19.
(184) O'Brien, R. J.; Xu, L.; Milburn, D. R.; Li, Y.; Klabunde, K. J.; Davis, B. H. *Top. Catal.* **1995**, *2*, 1.
(185) Pratt, S. J.; King, D. A. *Surf. Sci.* **2003**, *540*, 185.
(186) Lee, J. S.; Kim, S.; Kim, Y. G. *Top. Catal.* **1995**, *2*, 127.
(187) Llorca, J.; Homs, N.; Sales, J.; Fierro, J. L. G. *J. Catal.* **2004**, *222*, 470.
(188) Santiesteban, J. G.; Bogdan, C. E.; Herman, R. G.; Klier, K. Mechanism of C_1-C_4 alcohol synthesis over alkali/MoS_2 and alkali/Co/MoS_2 catalysts. *Proceedings of the 9th International Congress on Catalysis*; Phillips, M. J., Ternan, M., Eds; 1988; Vol. 2 C1 Chemistry, pp 561.

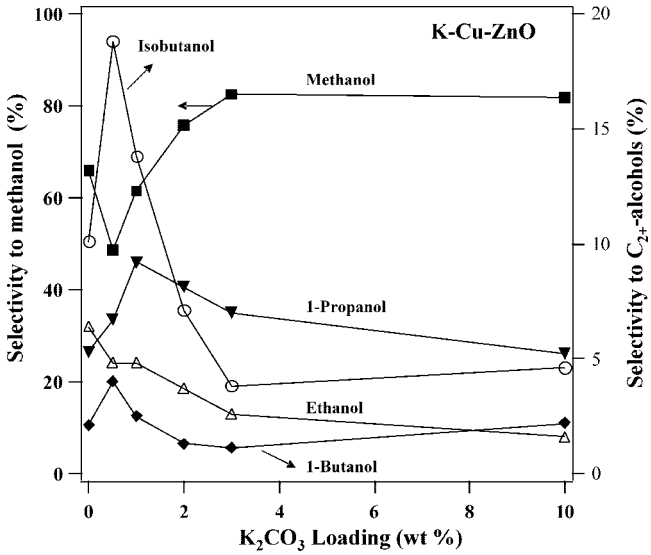

Figure 11. Effect of alkali promoter (K_2CO_3) loading on Cu–ZnO-based methanol synthesis catalysts on alcohol selectivity.[100]

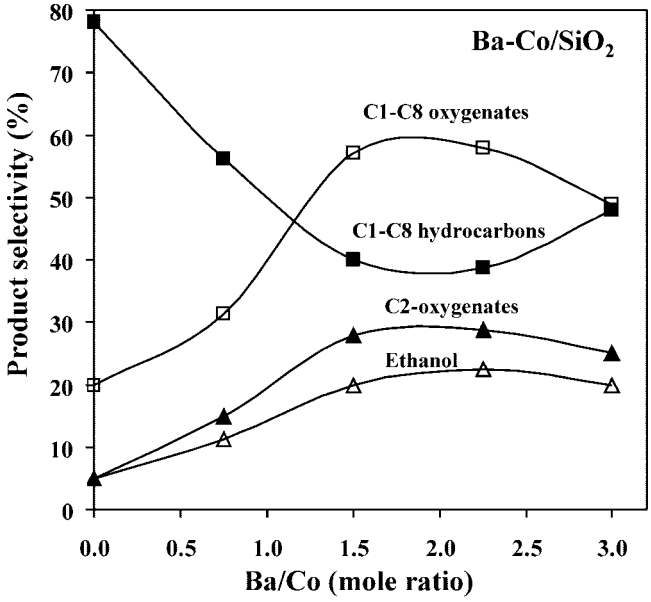

Figure 12. Effect of alkali (Ba)/Co ratio on product selectivity over Ba-promoted Co/SiO_2 Fischer–Tropsch-type catalyst.[120]

the added alkali can reduce the active hydrogen availability or activity by blocking the active sites for dissociative adsorption of CO, thereby decreasing the interaction between CO and the catalyst surface. The associatively adsorbed CO will be directly hydrogenated to alcohols. It has been observed that the addition of alkali promoters increases higher alcohol production in the order of Li < Na < K < Cs < Rb, the same order as their basicity. In some cases, alkaline earth metals such as Sr and Ba have also been used as promoters. Catalyst doping with a small amount of alkali usually increases the reaction rate. Excess alkali loading might block the active sites on the catalyst surface and lose the BET surface area, leading to activity loss.

The effects of alkali loading on the selectivity of ethanol and higher alcohols over selected Cu/ZnO-based, $ZnO–Cr_2O_3$-based, and MoS_2-based catalysts are shown in Figures 11, 12, and 13, respectively.[100,120,188] The results indicate that increasing K_2CO_3 loading on Cu–ZnO-based catalyst decreases the ethanol selectivity (Figure 11).[100] The methanol selectivity decreases initially and shows a minimum at about 1 wt % K_2CO_3 loading with concomitant increase in the selectivity of C_{3+} higher

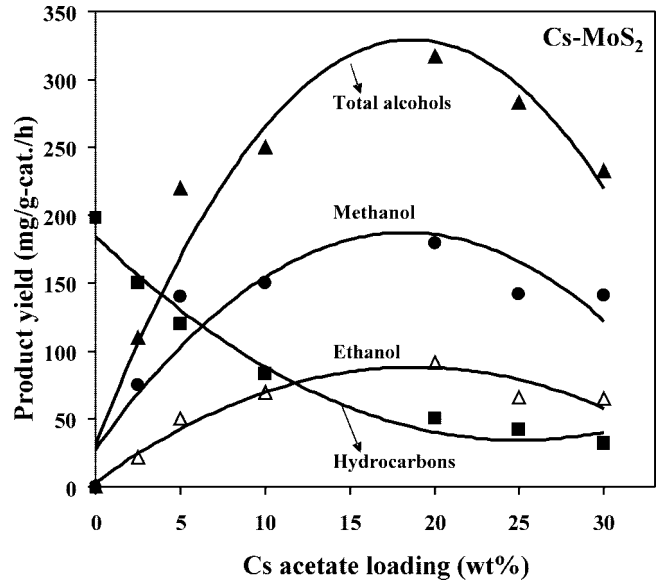

Figure 13. Effect of alkali (Cs acetate) loading on product yield over MoS_2-based catalyst.[188]

alcohols such as 1-propanol, 1-butanol, and isobutanol. It can be seen that the added alkali improves the selectivity of isobutanol dramatically compared to other higher alcohols. Similar results have also been observed over other Cu–ZnO-based low-temperature methanol synthesis catalysts as well as on $ZnO–Cr_2O_3$-based high-temperature methanol synthesis catalysts, although the alkali content to achieve the maximum isobutanol selectivity varied between 1 and 3 wt %.[94,97,189] Aquino and Cobo[130] also observed a decrease in productivity of $C_1–C_5$ linear alcohols upon loading of about 0.6, 2.0, 3.4, and 11 wt % Li, Na, K, and Cs on Cu–Co-based catalysts supported on Al_2O_3. Tien-Thao et al.[137] have observed a slight increase in productivity of $C_1–C_2$ alcohols when a very small amount of alkali such as Li, Na, K, Rb, and Cs is present in the Cu–Co-based perovskite catalysts tested in the syngas conversion to higher alcohols. Among the alkali tested, K exhibited relatively higher ethanol productivity. However, the effect of alkali loading on the productivity of isobutanol is not reported in these publications. The observed results suggest that both methanol and ethanol are precursors for the formation of C_{3+} alcohols over methanol synthesis catalysts. Methanol and ethanol, once formed, can undergo dehydrogenation to formaldehyde and acetaldehyde, respectively, which by aldol-type condensation over basic sites provided by alkali, can produce C_{3+} alcohols. This aspect will be discussed in more detail in section 5.2.2.

In contrast to Cu–ZnO- and $ZnO–Cr_2O_3$-based catalysts, increasing alkali loading in modified FT synthesis catalysts such as Co/SiO_2 (Figure 12)[120] and $Co–Mo/Al_2O_3$[153] and in MoS_2-based catalysts (Figure 13)[188,190] generally increases the yield and selectivity toward higher alcohols, including ethanol. In these catalysts, the addition of alkali helps suppress hydrocarbon formation with concomitant increase in the productivity of alcohols and oxygenates. This observation suggests that ethanol and higher alcohols are formed over these catalysts by a different pathway (possibly by CO insertion rather than aldol-type condensation). However, as reported for Cu–ZnO-based catalysts, the maximum alcohol productivity has been observed at

(189) Nuan, J. G.; Bogdan, C. E.; Klier, K.; Smith, K. J.; Young, C. W.; Herman, R. G. *J. Catal.* **1989**, *116*, 195.
(190) Lee, J. S.; Kim, S.; Lee, K. H.; Nam, I.; Chung, J. S.; Kim, Y. G.; Woo, H. C. *Appl. Catal. A: General.* **1994**, *110*, 11.

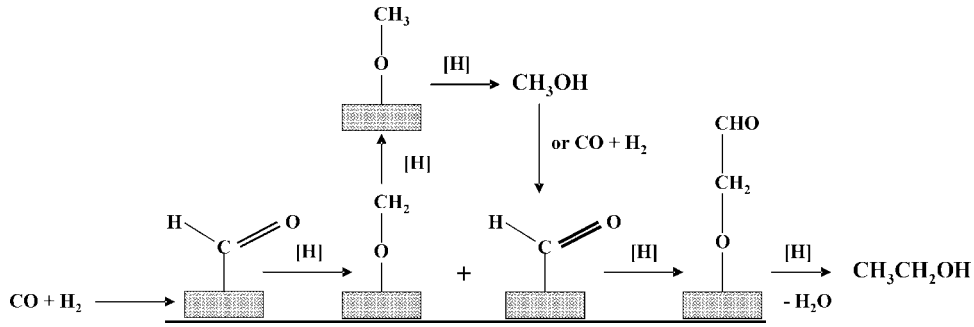

Figure 14. Ethanol formation by CO hydrogenation via a chain-growth mechanism over modified methanol synthesis catalysts.

an alkali loading of below 10 wt % in modified FT synthesis catalysts while a higher alkali loading of up to as much as 20 wt % seems beneficial over MoS_2-based catalysts (see Figure 13). Hence, it can be concluded that alkali promotion improves the ethanol yield over Cu–ZnO-based or ZnO–Cr_2O_3-based methanol synthesis catalysts to a small extent, while modified FT synthesis and MoS_2-based catalysts require an optimum alkali loading to achieve a maximum selectivity for ethanol and higher alcohols.

5.2.1.2.3. Effect of CO_2 in the Feed. As can be noted from Table 1, the syngas derived from biomass consists of significant amount of CO_2 (up to about 25% depending upon the type of gasifier employed). There will be a process incentive if the syngas containing CO_2 can be used as a feedstock for the production of ethanol and mixed alcohols, as this can avoid the upstream CO_2 removal step, and can reduce the cost of the overall process. However, the catalysts to be employed for ethanol and mixed alcohols synthesis should be capable of tolerating such a large CO_2 concentration in the syngas feed.

The effect of CO_2 in the feed on the catalytic performance of methanol synthesis catalysts has been studied in detail, and different conclusions have been reached. Klier et al.[191] have reported that CO_2 has a promoting role in methanol synthesis over Cu–ZnO-based catalysts especially at lower CO_2 levels (2–4%). The activity gradually decreases with further increase in CO_2 concentration in the feed. On the other hand, Chinchen et al.,[192] based on ^{14}C tracer technique experiments on similar Cu–ZnO-based catalysts, demonstrated that CO_2 is the source of methanol and is formed via formate intermediates which upon hydrogenation produce methanol.

Very little information is available on the effect of CO_2 on higher alcohol synthesis catalysts. Calverley and Smith,[101] by comparing the performance of unpromoted and 0.5% K_2CO_3-promoted catalysts, reported that the higher alcohols yield passes through a maximum around 4% CO_2 in the feed over both the catalysts. The catalyst promoted with 4% K_2CO_3 is less active for both methanol and higher alcohols production when CO_2 is present in the feed. Forzatti et al.[47] have reported that the higher alcohol productivity is markedly depressed by the presence of CO_2 in the feed over 15% Cs_2O loaded on ZnO–Cr_2O_3 catalyst. The inhibiting role is primarily associated with the formation of isobutanol, the terminal product of the higher alcohols synthesis reaction, rather than ethanol and C_2-oxygenates.

The effect of CO_2 on CuCo-based catalysts also has not been well-understood. However, it should be noted that the syngas used in the IFP process always contained about 13% CO_2 in the feed.[138,139] The alkali modified CuCo-based catalysts employed in this process exhibited relatively higher yields of ethanol and C_{3+} alcohols (see data in Table 7). On the other hand, Boz[131] reported that increasing the CO_2 content from 0 to 10% at the inlet reduced the selectivity for higher alcohols.

The MoS_2-based catalysts are reported to be less sensitive to CO_2 in the feed stream than other HAS catalysts although no quantitative data are available to compare and understand the effect of CO_2 on ethanol productivity.[50] Gang et al.[165] reported a decrease in C_{2+} alcohols productivity with increasing CO_2 concentration in the feed. However, the presence of CO_2 in the feed can cause greater amounts of water to be formed via the reverse water–gas shift reaction and can reduce the formation of CO_2. The water formed can poison the catalyst surface due to competitive adsorption.

5.2.1.2.4. Reaction Mechanism. The mechanism of higher alcohols synthesis over non-noble metals-based catalysts is more complex than that discussed for Rh-based catalysts. Depending on the type of metals and promoter used, several series of steps such as CO adsorption (associative/dissociative), hydrogenation of the adsorbed CO to formyl species, aldol-type condensation or CO insertion to form a C–C bond followed by hydrogenation of the intermediate species to produce alcohols, oxygenates, and hydrocarbons could occur.

On the basis of results published by various research groups, a generalized mechanism for the formation of ethanol over Cu-based catalyst has been proposed as shown in Figure 14. In this mechanism, an adsorbed formyl species can be formed from CO and H_2. If CO_2 is present in the feed, the adsorbed formyl species could be formed via an adsorbed formate species. Hydrogenation of the adsorbed formyl species to formaldehyde, followed by subsequent hydrogenation, produces methanol. The adsorbed formyl species can react with another adsorbed formyl species (formed either from syngas or from methanol) to produce an adsorbed acetyl species. Subsequent hydrogenation of the adsorbed acetyl species can produce ethanol. The acetyl intermediate can further react with another formyl species to form propanol or with another acetyl species to form butanol by an aldol-type condensation reaction over the basic catalyst surface. The decrease in ethanol productivity with increasing alkali content supports the involvement of aldol-type condensation reactions over alkali-promoted Cu-based catalysts. The chain growth generally terminates at isobutanol over Cu-based catalysts.

On the other hand, ethanol can be formed by the CO insertion mechanism over MoS_2-based and modified FT synthesis catalysts, as shown in Figure 15. Hydrogenation of the adsorbed formyl species formed by the adsorption of syngas can produce adsorbed alkyl species. CO insertion into the metal–alkyl bond can form an acyl intermediate, which upon hydrogenation can

(191) Klier, K.; Chatikavanji, V.; Herman, R. G.; Simmons, G. W. *J. Catal.* **1982**, *74*, 343.
(192) Chinchen, G. C.; Denny, P. J.; Parker, D. G.; Spencer, M. S.; Whan, D. A. *Appl. Catal.* **1987**, *30*, 333.
(193) Vanderspurt, T. H.; Greaney, M. A.; Leta, D. P.; Koveal, R. J.; Disko, M. M.; Klaus, A. V.; Behal, S. K.; Harris, R. B. *Isobutanol synthesis catalyst*. U.S. Patent No. 6,034,141, March 2000.

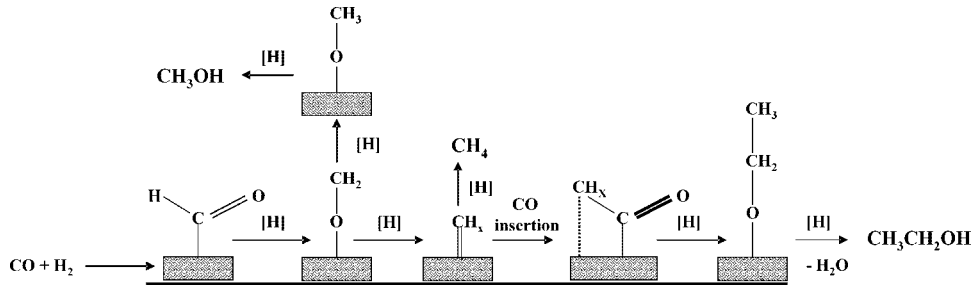

Figure 15. Ethanol formation by CO hydrogenation via a CO insertion mechanism over modified Fischer–Tropsch synthesis and MoS_2-based catalysts.

produce ethanol. Methane and higher hydrocarbons can be formed by hydrogenation or reaction with another adsorbed alkyl species, respectively.

5.2.2. Methanol Homologation. 5.2.2.1. Catalysts. The direct synthesis of C_{2+} alcohols from syngas indicates that the C–C bond formation in the first step to transform C_1 to C_2 species is the most difficult and rate-determining step. In order to enhance the reactivity of the C_1 intermediate that is formed from syngas, lower alcohols such as methanol and ethanol have been added to the feed. The added alcohol reacts with C_1 intermediates on the catalyst surface to produce higher alcohols. This strategy has been used in the past mostly for the synthesis of isobutanol by cofeeding either methanol or ethanol. The carbon chain growth enhanced by cofeeding methanol is referred to as methanol homologation, which on certain catalysts leads to the formation of ethanol with high yield and selectivity.

The methanol homologation to ethanol has been investigated as early as 1951 when Wender et al.[67] used cobalt carbonyl homogeneous catalyst as discussed in section 5.1. Following this work, a large number of patents have been filed for the synthesis of ethanol using either homogeneous catalysts or heterogeneous catalysts in the liquid phase. In 1979, Bartish[194] reported the use of Co-based and CoRh-based heterogeneous catalysts for this reaction. The reaction performed in the liquid phase in the temperature range between 180 and 200 °C and in the pressure range around 5000 psig using a H_2/CO ratio between 1 and 2 exhibited an ethanol yield of 7–10%, with over 70% ethanol selectivity. Hargis and Dubeck[195,196] have reported the use of alkali-promoted Rh–Fe bimetallic catalyst supported on Al_2O_3 for the synthesis of a mixture of ethanol and methyl acetate. The methanol homologation reaction performed in a fixed-bed reactor at 275 °C and 220 psig with a GHSV of 1800 showed about 46% ethanol selectivity with a carbon conversion of about 3%. The catalyst contained 8.3% $Ca(OA)_2$, 3.3% Rh–3.4% Fe supported on Al_2O_3. They have also reported that addition of a heterocyclic amine promoter such as pyridine to $RhFe/Al_2O_3$ catalyst improved the ethanol yield significantly, probably due to enhancement of basicity of the catalyst.

Methanol homologation to ethanol together with a wide range of acetate and ether over lanthanum hydroxide at 390 °C and 600 psig has also been reported.[197,198] The ethanol selectivity was about 20% among the homologation products observed. Mazanec et al.[199] have reported the reaction over ThO_2 promoted by K and Cs. At 400 °C and 1000 psig pressure, the catalyst exhibited about 22% methanol conversion into higher alcohols; however, the selectivity and yield of ethanol are not reported.

The reaction has also been investigated over unpromoted and alkali-promoted Cu-based catalysts, either by cofeeding methanol along with syngas[93,101,102,104,107,197,200–210] or by conducting the syngas conversion reaction in a dual-bed reactor, wherein the methanol formed from syngas in the first catalytic bed is subsequently converted into ethanol and higher alcohols in the second bed.[93,107] The dual-bed approach produced isobutanol as the predominant product with small amount of ethanol.

Xu and Iglesia[206] have studied the methanol homologation reaction over Cs-promoted $Cu–ZnO–Al_2O_3$ and K-promoted $Cu–MgO–CeO_2$ catalysts. The observed ethanol yield of 17 mg/(g cat h) was an order of magnitude higher than the yields of 1-propanol and isobutanol on the Cs-promoted catalyst. The ethanol formation was found to increase with increasing residence time. The K-promoted catalyst exhibited poor performance compared to the Cs-promoted catalyst.

A few selected heterogeneous catalysts employed in the methanol homologation reaction performed in fixed-bed reactors are listed Table 10. Under the experimental conditions employed in these studies, an ethanol yield between 18 and 50 mg/(g cat h) has been obtained. This is significantly lower than that obtained in the direct conversion route over some of the catalysts reported in Tables 5 and 7. However, under the given set of experimental conditions, methanol cofeed has been found to increase the yields of higher alcohols, including ethanol.[200–210] Ethanol yield could be further improved by performing the methanol reductive carbonylation reaction under a set of suitable experimental conditions. These experimental conditions should be identified and optimized for the given catalyst type.

The Gridley ethanol demonstration project utilizing biomass gasification technology has been reported recently.[49] This process involves the gasification of biomass, especially rice straw, into syngas, followed by catalytic conversion of syngas

(194) Bartish, C. M. *Synthesis of ethanol by homologation of methanol*. U.S. Patent 4,171,461, October 1979.
(195) Hargis, D. C. Dubeck, M. *Catalytic composition for the selective formation of ethanol and methyl acetate from methanol and synthesis gas*. U.S. Patent 4,309,314, January 5, 1982.
(196) Hargis, D. C.; Dubeck, M. *Ethanol from methanol and synthesis gas*. U.S. Patent 4,370,507, January 1983.
(197) Fenton, D. M. *Homologation of alkanols*. U.S. Patent 4,540,836, September 1985.
(198) Mazanec, T.; Geoden, G. V.; Frye, J. G., Jr. *Process for the production of alcohols*. U.S. Patent 4,608,447, August 26, 1986.
(199) Mazanec, T. J. *J. Catal.* **1986**, *98*, 115.
(200) Lin, J.; Knifton, J. F. Production of ethanol from methanol and synthesis gas, U.S. Patent 4,409,405, Oct. 1983.
(201) Calverley, E. M.; Smith, K. J. *Stud. Surf. Sci. Catal.* **1992**, *73*, 111.
(202) Hilmen, A.-M.; Xu, M.; Gines, M. J. L.; Iglesia, E. *Appl. Catal., A* **1998**, *169*, 355.
(203) Cosimo, J. I. D.; Apesteguia, C. R.; Gines, M. J. L.; Iglesia, E. *J. Catal.* **2000**, *190*, 261.
(204) Gines, M. J. L.; Iglesia, E. *J. Catal.* **1998**, *176*, 155.
(205) Lachowska, M. *React. Kinet. Catal. Lett.* **1999**, *67*, 149.
(206) Xu, M.; Iglesia, E. *J. Catal.* **1999**, *188*, 125.
(207) Egmond, C. F. V.; Argo, A.; Xu, T.; Janssen, M. J.; Sher, J. *Methanol and ethanol production for oxygenate to olefin reaction system*. U.S. Patent No. 7196239, March 2007.
(208) Miller, J.; Nevitt, T. D. *Process for producing higher alcohols or paraffins from synthesis gas*. U.S. Patent No. 5,169,869, 1992.
(209) Meitzner, G.; Iglesia, E. *Catal. Today* **1999**, *53*, 433.
(210) Robbins, J. L.; Iglesia, E.; Kelkar, C. P.; Derites, B. *Catal. Lett.* **1991**, *10*, 1.

Table 10. Selected Catalysts for the Synthesis of Ethanol via Methanol Homologation Reaction

	experimental conditions						STY (mg/(g cat h))				
catalyst	temp (°C)	press (psig)	GHSV (h^{-1})	H_2/CO	CO/MeOH	X_{CO}[a] (%)	C_2-OH	C_3-OH	iC_4-OH	other oxygenate	ref
8.3% $Ca(OAC)_2$–3.3% Rh–3.4% Fe/γ-Al_2O_3	250	220	1800	1.0	1.0	2.6	43.3	NA	NA	NA	194
	275	220	1730	1.0	1.1	3.2	46.5	NA	NA	NA	194
ZrO_2/ZnO/MnO/K_2O/Pd	400	3626	99000	1.0	6.9	NR	48	69	258	41	48
ZrO_2/ZnO/MnO/K_2O/Pd[b]	400	3626	99000	1.0	15.8	NR	271	171	172	28	48
Cs–Cu/ZnO/Al_2O_3	265	290	5050	1.0	77	<1	18.4	7.2	4.4	NA	205
Cs–Cu/ZnO/Cr_2O_3	275	1102	≈3500	0.45	≈8	NR	35.3	14.8	18.2	16.2	102

[a] X_{CO} = CO conversion; C_1-OH = methanol; C_2-OH = ethanol; alc STY = space time yield of alcohol; NA = data not available. [b] Reaction was performed in a continuous stirred-tank reactor (CSTR), while all other data were obtained in a fixed-bed reactor.

to ethanol using proprietary FT catalysts developed by Pearson Technologies. Although detailed information on catalyst compositions and their performance is not known, the report states that the process produces a range of alcohols and that they are separated in a distillation column to produce 95% ethanol. Subsequent purification in a silica gel column produces 99% fuel-grade ethanol. The research also suggests that, in order to increase the ethanol yield, it is necessary to separate methanol byproduct by distillation and reintroduce it with the syngas at the compression stage. A complete conversion of methanol to ethanol in the FT reactor would require recycling of methanol up to 7 or 8 times.

5.2.2.2. Reaction Mechanism. Isotopic tracer technique studies using a mixture of $^{13}CO/H_2/^{12}CH_3OH$ over Cs-promoted Cu/ZnO/Al_2O_3 and K-promoted Cu/MgO/CeO_2 catalysts revealed that ethanol formation occurs via two different pathways: either by the insertion of CO into methanol followed by hydrogenation (*methanol reductive carbonylation*; eq 2) or by coupling of two methanol molecules, also referred to as methanol bimolecular reaction (eq 8).[189,199,201,206]

According to these reports, CO insertion and hydrogenation occurs over unpromoted and K-promoted CuO–ZnO-based catalysts. On the other hand, bimolecular reaction of methanol occurs over Cs-promoted CuO–ZnO-based catalysts. It has also been proposed that the formation of adsorbed formyl species occurs at a faster rate from methanol than from syngas. Nucleophilic attack of the formyl species on adsorbed formaldehyde species of another methanol and subsequent hydrogenation lead to the formation of ethanol.

The involvement of formaldehyde and adsorbed formyl species as an intermediate for the synthesis of ethanol from methanol or from a mixture of methanol and syngas has been shown clearly by Kiennemann, et al.[211] These authors have studied the mechanism of ethanol and higher alcohols synthesis over Cu–ZnO–Al_2O_3 catalysts by temperature programmed desorption (TPD) of various probe molecules such as methanol, formaldehyde, ethylene, glycol, ethanol, acetone, and propionaldehyde. Addition of methanol as a probe molecule in a syngas (H_2/CO = 2) flow desorbed, in increasing order, 1-propanol, ethanol, and isobutanol (Figure 16). Formation of products that are characteristic of isobutylic synthesis stopped when CO was removed from the feed. In contrast to these observations, the order of desorption of alcohols was reversed and ethanol was desorbed as the major component when formaldehyde, instead of methanol, was used as a probe molecule (Figure 17). These results are very interesting and clearly suggest that formaldehyde is the primary intermediate in the formation of ethanol. The observed results have been attributed to the involvement of formaldehyde in two parallel

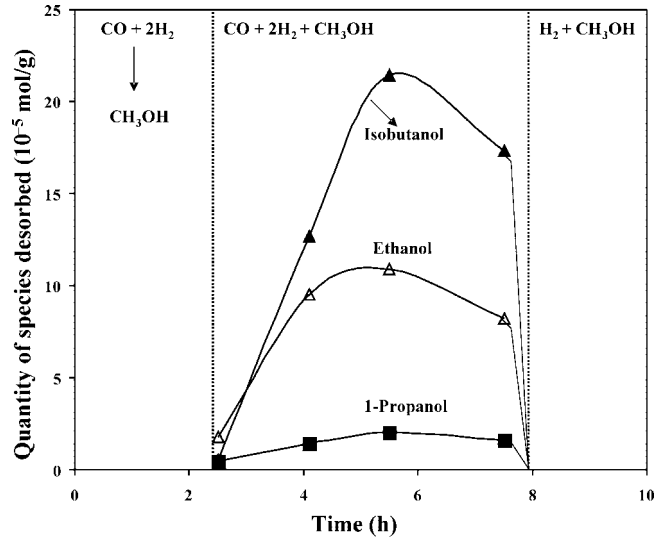

Figure 16. Effect of methanol addition as a probe molecule in a CO + $2H_2$ flow on alcohol production observed in temperature programmed desorption.[221]

reactions, namely the dimerization and CO insertion into a metal-adsorbed formaldehyde bond.

Base-catalyzed self-condensation of formaldehyde to glycoaldehyde is known in the literature.[212,213] Subsequent hydrogenation of glycoaldehyde can produce ethanol as shown in eqs 11 and 12, respectively.

$$2HCHO \rightarrow HOCH_2CHO \quad (11)$$

$$HOCH_2CHO \rightarrow CH_3CH_2OH \quad (12)$$

Over Cs-doped Cu–ZnO and Cu–ZnO–Al_2O_3 catalysts, Nuan et al.[189,202] have reported the formation of the first C–C bond in ethanol via coupling of two C_1 intermediates originating from methanol.

Glycoaldehyde can also be formed by the insertion of CO in formaldehyde followed by hydrogenation over Rh-based catalysts. In fact, ethylene glycol has been produced by the reaction of formaldehyde with syngas as shown in eqs 13 and 14.[211,213]

$$HCHO + CO + H_2 \rightarrow HOCH_2CHO \quad (13)$$

$$HOCH_2CHO + H_2 \rightarrow HOCH_2CH_2OH \quad (14)$$

Based on these results, plausible mechanisms for the reductive carbonylation and bimolecular reactions of methanol have been proposed as shown in Figures 18 and 19, respectively. In both cases, the participation of formaldehyde species formed from methanol has been shown.

(211) Kiennemann, A.; Idriss, H.; Kieffer, R.; Chaumette, P.; Durand, D. *Ind. Eng. Chem. Res.* **1991**, *30*, 1130.

(212) Gracey, et al. U.S. Patent No. 5097089, 1992.

(213) Tajima, *J. Comput. Chem. Jpn.* **2003**, *2*, 127.

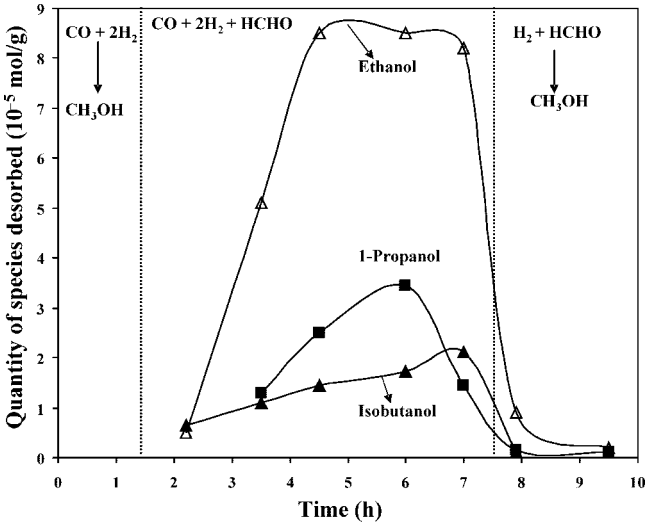

Figure 17. Effect of formaldehyde addition as a probe molecule in a CO + $2H_2$ flow on alcohol production observed in temperature programmed desorption.[221]

Unlike methanol reductive carbonylation, which has been studied extensively as discussed above, the bimolecular reaction of methanol to form ethanol has been shown mostly by surface techniques such as isotopic tracer techniques and TPD, although the thermodynamic analysis shown in Figure 6 indicates that the reaction is much more favorable than the reductive carbonylation reaction. Fox et al.[214] have observed that when methanol vapors were passed through metal acetylides such as CaC_2, Na_2C_2, CeC_2, and LaC_2, a mixture of higher alcohols, including ethanol and isobutanol with high selectivity to isobutanol were obtained. On the basis of ^{13}C labeling studies, the authors have confirmed that higher alcohols are formed from methanol rather than metal acetylides. The authors have proposed base-catalyzed aldol-type condensation of aldehydes, including formaldehyde, as the key chain-growth species.

On the other hand, the methanol-coupling reaction is well-known in the methanol to olefin (MTO) and methanol to gasoline (MTG) processes performed over zeolite-based acidic catalysts wherein the initial C–C bond formation to form ethanol is being considered as the rate-determining step.[215,216] Thus, the mechanism of initial C–C fond formation for the conversion of methanol to ethanol over zeolite-based catalysts has been investigated in more detail, both experimentally and theoretically.

5.2.3. Hydrogenation of CO_2. Hydrogenation of CO_2 appears to be another possible approach for the synthesis of ethanol with high yield (eq 15).[89,217–220]Hydrogenation of CO_2 to methanol has already been studied over Cu-based and noble metal-based catalysts.[89,221] Research on the catalytic conversion of CO_2 to value-added chemicals attracted increasing interest in recent years as a means of mitigating the emission of this greenhouse gas.[3]

$$2CO_2 + 6H_2 \rightarrow CH_3CH_2OH + 3H_2O \quad (15)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (16)$$

CO_2 is relatively inactive molecule, but undergoes reduction with H_2 to produce CO, the highly active molecule by reverse water–gas-shift (r-WGS) reaction (eq 16). The CO produced is subsequently hydrogenated to the desired product. Inui and co-workers[217–219] have reported polyfunctional composite catalysts for the hydrogenation of CO_2 to ethanol with a high ethanol yield. They designed catalysts containing functions for three different elementary steps involving (i) reduction of CO_2 to CO, (ii) C–C bond formation, and (iii) –OH group insertion. A series of Rh-based supported catalysts, Fe-based FT catalysts, Cu-based methanol synthesis catalysts, and a combination of them in different ways, either by physically mixing or by conducting CO_2 hydrogenation reactions in a dual-bed reactor, have been reported. A high space time yield (STY) of ethanol between 300 and 500 g/(L cat h) (Table 11) has been obtained at a GHSV of 20 000 h^{-1}. The ethanol yield further increased to about 800 g/(L cat h) when the GHSV was increased to 50 000 and 70 000 h^{-1}. The authors claim that the ethanol STY obtained in these studies is an order of magnitude higher than that normally obtained in the industrial production of ethanol by the ethylene hydration route.

Hu et al.[89] have also used similar catalyst compositions and a Pd–ZnO/Al_2O_3 catalyst for the hydrogenation of CO_2 to ethanol, but the reactions have been performed in microchannel reactors. These authors have also shown a high yield of ethanol between 300 and 400 g/(L cat h).

Although the reaction produced ethanol with high yield, the selectivity to ethanol is poor, below 20%, and this is due to the formation of a large amount of hydrocarbons (50–70%) as byproducts. It is unclear from these reports if these hydrocarbons are gaseous or liquids. In any case, the results shown in these publications are interesting because the reaction produces primarily methanol and ethanol as major oxygenates, with ethanol production being significantly higher than methanol production. Further improvement in ethanol selectivity may be possible by suppressing the hydrocarbon selectivity by suitably modifying the catalyst compositions and optimizing the reaction operating conditions. However, this process may not be commercially viable as the process requires pure H_2, which is very expensive. Furthermore, the process produces 3 mol of water for each mole of ethanol produced (eq 15), resulting in the production of aqueous ethanol with lower concentration, which may add cost for the separation of ethanol from water. A novel catalytic process that can convert syngas containing a large amount of CO_2 (10–30%) into ethanol with high yield, in the range reported by these authors may be more practical.

6. Reactor Design

The syngas to ethanol conversion reactions are highly exothermic, with heats of the reaction varying between −70 and −270 kJ/mol of ethanol (Figure 4), depending on the reaction pathway. Heat must be removed during the reaction to achieve high activity, selectivity, and longer catalyst lifetime. Consequently, designing a suitable reactor is critical to achieving higher yields and selectivities of the desired alcohol products. Most of the laboratory and bench-scale studies discussed above employed fixed-bed flow reactors, whereas few studies have used slurry reactors, such as CSTRs and slurry bubble column reactors (SBCRs). Pilot-plant studies of higher alcohols synthesis also used a series of fixed-bed adiabatic reactors with interstage condensation.

(214) Fox, J. R.; Pesa, F. A.; Curatolo, B. S. *J. Catal.* **1984**, *90*, 127.
(215) Blaszkowski, S. R.; van Santen, R. A. *J. Am. Chem. Soc.* **1997**, *119*, 5020.
(216) Lo, C.; Giurumescu, C. A.; Radhkrishanan, R.; Trout, B. L. *Mol. Phys.* **2004**, *102*, 281.
(217) Inui, T. *Catal. Today* **1996**, *29*, 329.
(218) Inui, T.; Yamamoto, T. *Catal. Today* **1998**, *45*, 209.
(219) Inui, T.; Yamamoto, T.; Inoue, M.; Hara, H.; Takeguchi, T.; Kim, J. *Appl. Catal. A: General* **1999**, *186*, 395.
(220) Okabe, K.; Yamada, H.; Hanaoka, T.; Matsuzaki, T.; Arakawa, H.; Abe, Y. *Chem. Lett.* **2001**, *904*.
(221) Melian-Cabrera, I.; Granados, M. L.; Fierro, J. L. G. *J. Catal.* **2002**, *210*, 285.

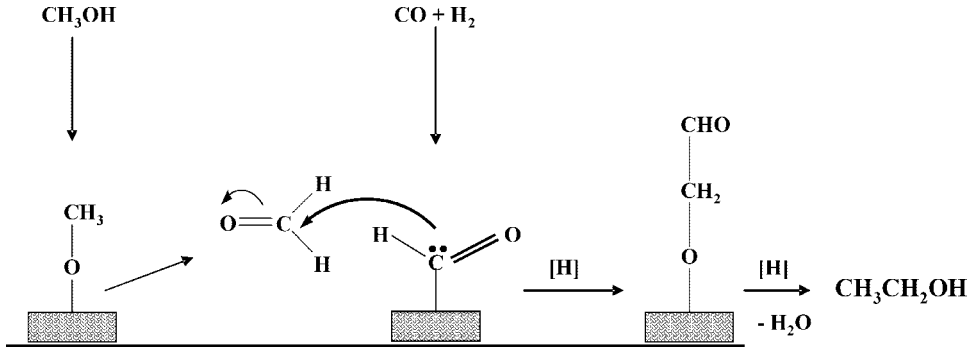

Figure 18. Plausible mechanism for the synthesis of ethanol via the methanol reductive carbonylation pathway.

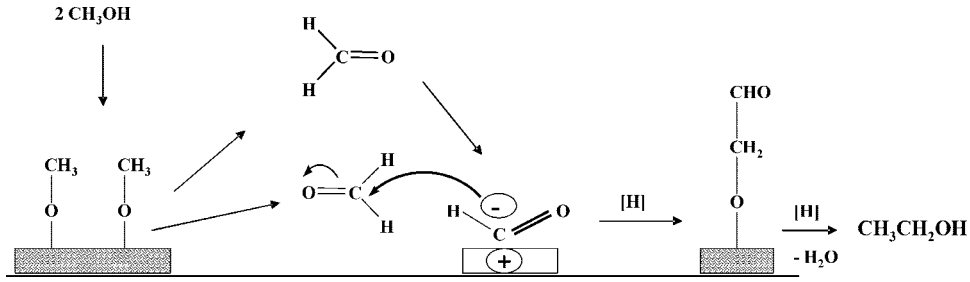

Figure 19. Plausible mechanism for the synthesis of ethanol via the methanol bimolecular reaction pathway.

Table 11. Yield and Selectivity of Ethanol in the Hydrogenation of CO_2 over Polyfunctional Composite Catalysts[218,219]

						carbon selectivity (mol %)					STY (g/(L cat h))	
catalyst	temp (°C)	press (psig)	GHSV (h^{-1})	H_2/CO_2	X_{CO2}[a] (%)	MeOH	EtOH	oxy	HC	CO	MeOH	EtOH
KCuFeAl + KCuFeAlGaPd[b]	330	1175	20000	3.0	47	5.8	17.4	NA	62.8	12.3	196	420
Pd(CuFeAlKGa + CuZnAlK)[b]	330	1175	20000	3.0	54.5	5.2	17.0	3.6	64.5	9.7	202	476
0.5Rh/SiO_2 + CuFeAlK[c]	350	1175	70000	3.0	29.4	2.9	9.3	0.5	46.7	40.6	335	787
CuFeAlK + CuZnAlK[b]	330	1175	50000	3.0	31.1	5.0	14.8	2.1	51.5	26.6	408	874

[a] X_{CO2} = CO_2 conversion; STY_{EtOH} = space time yield of ethanol; S_{EtOH} = selectivity of ethanol; oxy = other oxygenates; HC = hydrocarbons; NA = data not available. [b] Catalysts were physically mixed in a 1:2 ratio. [c] Catalysts were packed in series with a weight ratio of 1:2.

Table 12. Comparison of Ethanol Yield (g/(L cat h)) Obtained in a Fixed-Bed Reactor and CSTR in the Direct Synthesis and Reductive Carbonylation Pathways over ZrO_2/ZnO/MnO/K_2O/Pd Catalyst[48] [a]

	Fixed-Bed Reactor (Pathway)				CSTR (Pathway)			
	direct synthesis (GHSV: h^{-1})		methanol reductive carbonylation (GHSV: h^{-1})		direct synthesis (GHSV: h^{-1})		methanol reductive carbonylation (GHSV: h^{-1})	
alcohol	27500	99000	275000	99000	27500	99000	275000	99000
methanol	1541	3770	*b*	*c*	467	1331	*d*	*d*
ethanol	17	60	12	48	134	320	128	271
1-propanol	26	75	20	69	75	179	80	171
isobutanol	272	377	109	258	79	150	97	172
2-methyl-butanol-1	39	61	20	41	20	32	20	28

[a] Reaction conditions: temperature 400°C; pressure = 3626 psig; CO/H_2 = 1. [b] 10.5 g/h of methanol was added to syngas. [c] 10.3 g/h of methanol was added to syngas. [d] 4.5 g/h of methanol was added to syngas.

A comparison of data obtained from fixed-bed and CSTRs collected under the same operating conditions over ZrO_2/ZnO/MnO/K_2O/Pd catalyst indicates that ethanol yield increases 5–10 fold in both the direct synthesis and in methanol reductive carbonylation reactions when the reaction is performed in a CSTR compared to a fixed-bed reactor (Table 12).[48] Furthermore, the reaction in a fixed-bed reactor produces isobutanol as the major C_{2+} alcohol in both the direct synthesis and methanol reductive carbonylation pathways. On the other hand, ethanol is produced as the major C_{2+} alcohol in a CSTR in both pathways. The use of a CSTR also decreases the methanol productivity. These results indicate the advantages of using a slurry reactor such as a CSTR for the conversion of syngas to ethanol. The observed difference in ethanol yield obtained between a fixed-bed reactor and CSTR could be due to efficient heat removal and backmixing, which favors the consecutive reactions of methanol, achieved in this reactor.

Slurry-phase reactors, such as SBCR, are considered to be the reactor of choice for carrying out highly exothermic reactions in commercial embodiments. Some of the advantages of slurry reactors over fixed-bed reactors are the following:

■ Simple heat removal by slurry circulation offers excellent temperature control leading to higher conversion per pass.

■ The use of smaller catalyst particles excludes extreme intraparticle mass transfer limitations.

■ Simple reactor design and scale-up using data from a set of experiments in a laboratory CSTR is possible.

■ A higher catalyst slurry concentration of 50 wt % or greater

Table 13. Selected MoS_2-Based Catalysts Reported for the Direct Conversion of Syngas To Ethanol and Mixed Alcohols[a]

	experimental conditions					carbon selectivity (%)[b]						alc STY (mg/(g cat h))		
catalyst	temp (°C)	press (psig)	GHSV (h^{-1})	H_2/CO	X_{CO} (%)	HC[c]	CO_2	C_1-OH	C_2-OH	C_{3+}-OH	EtOH	$\Sigma_{alcohol}$	ref
6% Rh 1.5% Mn/SiO_2[d,e]	300	783	3750	2.0	40.5	48.1	3.4	1.9	44.5	NA	NA	NA	88
K_2O–Pd–ZrO_2–ZnO–MnO[f]	400	3626	99000	1.0	NA	NA	NA	NA	NA	NA	320	2112	48
3 mol % Cs–Cu–ZnO–Cr_2O_3	325	1100	18000	0.75	11.7	NA	NA	NA	NA	NA	69	1547	92
$Cu_{1.0}Co_{1.0}Cr_{0.8}K_{0.09}$ + cement	250	1740	8000	2.0	NA	NA	NA	NA	NA	NA	341	729	138
K–Co–β-Mo_2C-10[g,h]	300	1160	2000	1.0	36.7	61.4	NA	11.3	13.9	24.0	NA	134	157
$K_2CO_3CoMoS_2$	270	2100	2546	1.1	10.4	12.7	1.7	48.2	29.6	7.8	NA	250	172
$Cs_2CO_3CoMoS_2$/clay	320	2000	4000	1.1	28.7	31.3	NA	10.8	30.3	22.0	NA	NA	179

[a] X_{CO} = CO conversion; HC = total hydrocarbons including methane; C_1-OH = methanol; C_2-OH = ethanol; C_{3+}-OH = all the alcohol products except methanol and ethanol; alc STY = space time yield of alcohol; $\Sigma_{alcohol}$ = sum of all the alcohols; NA = data not available. [b] Carbon selectivity is defined as the selectivity of all the carbon-containing products formed from converted carbon, and the values are recalculated from the original reported data. [c] HC = hydrocarbon selectivity calculated from the alcohol selectivity data. This may include CO_2 selectivity. [d] Other products are oxygenates. [e] A microchannel reactor was used. [f] A CSTR was used. [g] Catalyst contained a K/Mo = 0.2 and used K_2CO_3 as a K precursor. [h] Mo/Co = 10.

is possible, which will allow the use of relatively smaller reactors with minimal mass transfer limitations.

■ Catalyst addition and withdrawal can be accomplished without process interruptions.

■ Two or more catalysts can be mixed to serve different functions.

■ Continuous renewal (washing) of the catalyst surface by the slurry liquid can potentially lead to extended life and higher activity.

As an example, Chem Systems has conducted a pilot-scale study of isobutanol synthesis in a slurry reactor using a 40% slurry of Cs-promoted Cu–ZnO–Al_2O_3 catalyst in a hydrocarbon oil at 120 atm (1764 psig) and 350 °C.[38] However, the choice of a suitable solvent and the effect of solvent on the catalytic performance are issues that need to be addressed regarding the use of slurry-phase reactors.

7. Summary of Literature Review

The following conclusions can be derived from this review on the conversion of syngas to ethanol and higher alcohols:

• Catalytic conversion of syngas to ethanol and higher alcohols has been studied for the past 90 years using homogeneous and heterogeneous catalysts, but none of the processes have been commercialized, although a few have gone to pilot scale.

• Higher selectivity to ethanol could be achieved with homogeneous catalysts, but a commercial process based on these catalysts requires extremely high operating pressures, complex catalyst recovery, and expensive catalysts, making their commercial application almost impractical.

• Rh-based heterogeneous catalysts promoted by Fe or Mn preferentially produce ethanol over other alcohols; the limited availability and high cost of Rh, and the insufficient ethanol yield, can make these catalysts unattractive for commercial application.

• Modified methanol synthesis and Fischer–Tropsch synthesis catalysts based on CuZn, CuCo, and MoS_2 have been evaluated in syngas conversion to mixed alcohols, and some of them have been used in pilot plant testing. The rates of ethanol and total alcohol production are significantly lower than those achieved in methanol synthesis (1300 to 1500 mg methanol/(g cat h)). Thus, significant improvements in the alcohol production rate must be achieved.

• Direct synthesis of ethanol and higher alcohols from syngas is thermodynamically feasible, but kinetically controlled.

• The linear homologation of C_1 to C_2 alcohol is the bottleneck in ethanol and HAS. Methanol homologation, by cofeeding either methanol or formaldehyde along with syngas over a suitably modified catalyst composition, appears to be a promising approach to produce ethanol with high yields and selectivity.

• The reactor designs that have been employed in HAS catalyst R&D (i) typically adapted standard fixed-bed reactor technology with specialized cooling designs used for methanol synthesis or FT synthesis of hydrocarbon and (ii) indicated that improved product yield and selectivity could be achieved by performing reactions in slurry reactors such as CSTRs due to efficient heat removal, temperature control, and backmixing.

8. Research and Development Needs

8.1. Catalyst Selection/Development. Catalytic synthesis of ethanol from syngas suffers from low yield and poor selectivity of the desired alcohol product due to the slow kinetics of the C_1–C_2 linear chain growth and fast chain growth to form C_{2+} alcohols. R&D work to improve the ethanol yield and selectivity should focus on developing a methodology for increasing the kinetics of the C_1–C_2 chain growth. Substantial research, as evidenced by countless journal articles, has been carried out on developing direct ethanol synthesis, HAS, and methanol homologation catalysts over the past 90 years or so. In this section, we identify the best catalyst candidates from past research and development that merit further research and development for ethanol and HAS.

Homogeneous catalysts based on noble metals may be rejected from further consideration because of the high cost of the noble metal catalysts and the difficulties associated with catalyst recovery and reuse. Some of the best-performing heterogeneous catalysts and reaction operating conditions discussed in this review are gathered in Table 13. Among them, the low yield combined with high cost and limited availability of Rh is sufficient to also eliminate Rh-based catalysts from further consideration, unless an extremely active catalyst containing a very small amount of Rh (e.g., 0.1 wt %) and/or a novel process that improves the ethanol yield are developed. Furthermore, the high-temperature K_2O–Pd–ZrO_2–ZnO–MnO catalyst that uses severe operating conditions (high temperature and very high pressure) may also be eliminated from consideration because of the following factors:

(1) Its high operating pressure is not compatible with the operating pressure envisioned for commercial and developmental biomass gasifiers.

(2) Its high operating temperature results in high selectivity for methane and isobutanol, but not for ethanol.

The above concerns leave the following classes of heterogeneous catalysts for further consideration:

- alkali-modified, low-temperature methanol synthesis catalysts based on $Cu–ZnO/Al_2O_3$
- alkali-modified CuCo-based modified FT catalysts
- alkali-modified MoS_2-based catalysts

It is noteworthy that formulations based on these three classes of catalysts have been used in pilot plants for HAS or are being considered as potential catalyst candidates for pilot plants to be constructed in the future. Among the three classes, the $Cu–ZnO/Al_2O_3$ catalyst shows the lowest ethanol yield but is highly selective toward alcohols compared to hydrocarbons, whereas the CuCo-based IFP catalysts exhibit a high ethanol yield but with lower selectivity. The MoS_2-based catalysts show relatively higher ethanol selectivity, but still lower ethanol yield.

Modifications need to be made to these baseline catalyst formulations to improve the yield and selectivity toward ethanol. Promoters that could be considered include (1) alkali metal to be used and its concentration in the catalyst and (2) the way promoters are loaded. K and Cs are the promoters commonly used alkali promoters in these catalytic systems, and both have shown to improve the ethanol yield and selectivity. While a low concentration (around or lower than 3 wt %) of alkali is sufficient in Cu-based methanol synthesis catalysts, the MoS_2-based catalyst may require a higher alkali loading, even up to 20 wt %. Hence, the concentration of alkali required for the given type of catalyst needs to be optimized.

In addition to alkali promoters, Group VII and Group VIII metals can also be used as a promoter to increase the activity, thereby increasing the ethanol yield. For example, Co and Pd additions have been shown to increase the rate of methanol homologation to ethanol. Methanol can be added to the feed via the recycling of a portion of the methanol in a commercial embodiment, or methanol that is formed in-situ can undergo both homologation and coupling reactions to produce ethanol. Mn is a known promoter for enhancing the production of ethanol and also significantly promotes ethylene formation, which can be hydrated to form ethanol by the known ethylene hydration process over a solid acid catalyst. The Co to Mo ratio has been shown to be an important parameter for both unsulfided and sulfided CoMo-based catalysts, with an optimum for alcohol production of 1 to 7.

High dispersion of the catalyst that has been shown to improve activity for HAS and is also a very important consideration in catalyst development. Catalysts containing nanoparticles of active metals should be prepared with high dispersion and with structural promoters to prevent sintering at reaction conditions. Catalyst preparation techniques will include impregnation and precipitation, procedures specifically designed to yield nanoparticles of the metals with high dispersion, such as deposition–precipitation using a special precipitating agent. Scalability and cost of catalyst preparation/modification is also an important consideration. Exotic methods of catalyst modification/preparation that cannot be easily scaled up using conventional commercial equipment should be avoided.

Although methanol homologation via reductive carbonylation reactions seems promising, suitable catalysts having multiple functions are required to improve the conversion and selectivity to ethanol.

8.2. Selection of Reactor and Operating Conditions. Temperature is one of the most critical reaction parameters to be considered. Reaction temperature significantly influences not only the rate of kinetically controlled (e.g., ethanol) and HAS reactions but can also have a profound effect on selectivity because side reactions (e.g., methanation) have activation energies that are different from the desirable reactions. Thus, to maximize selectivity to ethanol, the temperature at maximum selectivity needs to be determined through experimentation and then closely controlled at this value in a commercial reactor.

The requirement for close temperature control can be met by suitable reactor choice and design. Choices include fixed-bed, fluidized-bed, and SBCR. Shell-, and tube-type, fixed-bed reactors can be employed to better control temperature. However, catalyst extrudates (typically 3/16 in.) have to be used for commercial applications whose internal temperature can be quite different from the gas temperature for exothermic reactions. These reactors are also hard to scale up. Fluidized-bed reactors use small catalyst particles and can provide for heat removal using boiler tubes placed in the bed; however, the catalyst particles need to be highly attrition-resistant. The use of an SBCR has significant advantages for the commercial embodiment of an ethanol and HAS process. The advantages include the following:

- finely dispersed catalyst in a heat-stable oil slurry at reaction temperatures of interest (250–325 °C);
- simple removal of heat using slurry circulation;
- excellent temperature control;
- simple design using data from a set of experiments in a laboratory CSTR;
- ease of scale-up and simple construction;
- 50 wt % or greater catalyst slurry possible to allow relatively smaller reactor with minimal mass transfer limitations;
- catalyst addition and withdrawal accomplished without process interruptions;
- ability to mix two or more catalysts to serve different functions;
- continuous renewal (washing) of the catalyst surface by the slurry liquid, potentially leading to extended life and higher activity.

The ability to mix a small amount of methanol-synthesis catalyst with an ethanol-synthesis catalyst in an SBCR could provide a novel approach to increasing ethanol selectivity via enhancement of the methanol homologation to ethanol.

Besides temperature, catalyst type and size, and reactor type, other important reaction parameters include feed H_2/CO ratio, gas hourly space velocity (contact time), pressure, and CO_2 and H_2O content of feed, as discussed below.

The feed H_2/CO ratio should be investigated to match what is available from current and emerging gasification processes that produce syngas. Due to differences in stoichiometry, the influence of this ratio will be different for the alcohol-forming, methanation, and WGS reactions. The involvement of WGS reaction will increase the actual H_2/CO ratio in the feed. Lower alcohols and hydrocarbons will be produced at high H_2/CO ratio and vice versa. H_2/CO ratios much lower than 1 could result in coke formation leading to catalyst deactivation.

Higher pressures will thermodynamically favor alcohol-forming and methanation reactions. In contrast, WGS thermodynamics will not be altered due to having no net change in moles for this reaction. The upper limit on pressure that can be used for the synthesis reactor will be dictated by the pressure of the gasifier producing the syngas (which is typically below 1000 psig) unless there is a provision to further compress the syngas.

Space velocity is another very important parameter. A higher space velocity will reduce the influence of secondary (or side) reactions and increase the productivity of alcohols. This will occur at the expense of CO conversion as Courty

et al.[55] demonstrated. As traditionally practiced for methanol synthesis, unconverted gases can be recycled to the synthesis reactor to maintain a high space velocity and low conversion per pass, leading to >95% CO conversion on the basis of the feed CO. Typical space velocities for commercial methanol syntheses in a water-cooled Lurgi reactor are in the 9000–10 000 h^{-1} range. This value includes recycling at a 4 to 1 recycle ratio and could be used as a starting point for ethanol synthesis.

Other components in the syngas feed besides H_2 and CO can also influence the synthesis reactions. Trace contaminants such as H_2S (except for the MoS_2-based catalysts), chloride, ammonia, and heavy metals (As, Se, etc.) must be removed to parts per billion (ppb) levels prior to the synthesis reactor to prevent catalyst poisoning. CO_2 and H_2O in the feed can also influence the alcohol-forming reactions. In fact, isotope tracer studies and industrial operations have led to an agreement within the research community that the presence of some CO_2 is necessary for the methanol synthesis catalyst to work, but its role in HAS is not clear.[23,136] In the absence of CO_2, basic sites along with Cu sites are required in methanol synthesis.[137] CO_2 can be present in the feed, or alternately, it can be generated via WGS using some steam in the feed. The activity for the methanol-synthesis catalyst passes through a maximum around 3–4 vol % CO_2 in the feed. Depending on the type of catalyst selected, the presence of some CO_2 may also be advantageous for ethanol synthesis.

9. Conclusions and Technical Challenges

No systematic study has been performed in the past to optimize ethanol synthesis from syngas and to efficiently integrate the synthesis and separation steps into an overall indirect liquefaction plant. Commercial success has been limited by low yield and selectivity, although a few pilot plants, ranging from 2 to 400 ton/d, have been built and operated for HAS. Syngas can be converted to ethanol directly using Rh-based catalysts; however, the Rh is very expensive, its availability is limited, and the yield is insufficient to justify its use. HAS, resulting in a mixture of C_1–C_5 alcohols, is a more desirable route, particularly when coupled with methanol homologation to increase the ethanol yield. HAS and methanol homologation catalysts are similar and consist of a combination of alkali-promoted base metals (e.g., Cu, Zn, Co, and Mo) on oxide supports. Catalysts of particular interest for further improvement include Cu–Co, unsulfided Co–Mo, and unpromoted and cobalt-promoted MoS_2. Current total alcohol yields from these catalysts are in the range between 100 and 600 g/(kg cat h), as compared to the benchmark 1300–1500 g/(kg cat h) methanol yield typically obtained in the commercially practiced methanol-synthesis process. Also, hydrocarbons, especially methane, and CO_2 are produced, thereby reducing total alcohol and ethanol selectivities.

The major technical challenge is to produce an ethanol-rich HAS product from biomass- and/or coal-derived syngas that will be cost competitive with corn-or petroleum-based ethanol. A systematic experimental process development and process integration study is needed to optimize ethanol synthesis from syngas and to efficiently integrate the synthesis and separation steps into an overall indirect liquefaction plant involving gasification, syngas cleanup, and syngas conversion.

Acknowledgment. The authors wish to thank the United States Department of Energy for financial support (Contract No. DE-FG36-GO85006). We are also grateful to several of our colleagues, especially Dr. Dharmesh Kumar, David Green, and Pradeep Sharma, for proof reading the manuscript, and Dr. Raghubir Gupta, the Director of the Center for Energy Technology at RTI, for his constant encouragement and support to prepare this review. RTI International is gratefully acknowledged for supporting this work.

EF700411X