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CONVERSION OF CELLULOSIC WASTES TO LIQUID HYDROCARBON FUELS: VOL. 4, SLURRY PHASE SYNTHESIS OF LIQUID HYDROCARBON FUELS FROM BIOMASS PYROLYSIS GAS USING IRON CATALYSTS: FINAL REPORT

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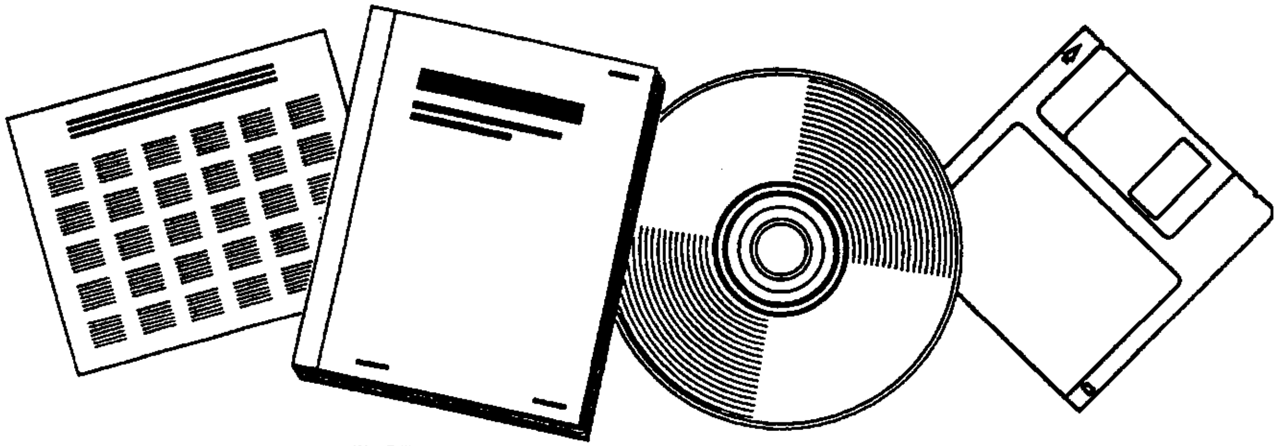

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ABSTRACT

An experimental assessment of liquids and iron based catalysts for use in a Fischer-Tropsch slurry reactor has been conducted. The best catalyst/liquid combination was found to be a 48Fe/4.8Cu/47.2Kieselguhr catalyst in Chevron Refined Wax 143. At the optimum operating conditions of 300°C, 200 psig, using a 5 weight % catalyst slurry with a molar H_2/CO feed ratio of 0.5, the yield of product was 118 mg/g-cat/hr.

Five different catalysts were tested in their ability to produce diesel type fuels from biomass pyrolysis gas. The catalysts tested, in order of decreasing product yield, were: kieselguhr supported, potassium promoted alumina supported, potassium promoted unsupported, unsupported, and alumina supported iron.

Two of the liquids tested, Syltherm 800 and Dow Corning 210H fluid, had a detrimental effect on catalyst activity. n-Hexadecane and n-eicosane were also tested, but their vapor pressures at synthesis temperatures were too high for practical use. Fischer-Tropsch product was tested successfully as a slurry liquid, but equipment modifications are required for the long term use of this liquid.

A two level factorial study using temperature, pressure, H_2/CO feed ratio, and catalyst concentration in the slurry as factors was also performed. Based on product yields, temperature was the most important factor, followed by the H_2/CO feed ratio, catalyst concentration, and pressure. Optimum operating conditions were located by fitting polynomials to the factorial study yields, and solving for the best operating conditions using classical optimization with constraint check.

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I. Introduction.

The production of diesel type transportation fuels from biomass feedstocks is an attractive alternative energy process. Biomass represents a large variety of renewable, low sulfur content cellulosic wastes such as sawdust, almond prunings, wheat straw, and forest residues. Urban wastes and crops grown specifically for their energy value are also potential feedstocks. Most other synthetic fuel projects require the use of coal.

There are two categories of biomass conversion processes: thermal and biological. In a typical biological process, microbes digest cellulose to produce methane as a product. Large reaction vessels and long processing times are required, and the processing is not always continuous. Thermal processing can be performed continuously in smaller reactors with residence times less than 1 second. A drawback to the thermal processes is their energy requirements, and the processing equipment is more complex than for biological methods.

The conversion process under investigation at Arizona State University is a two step gasification/ liquefaction process. The biomass is gasified using a thermal process, pyrolysis. The biomass is pyrolyzed to gaseous hydrocarbons, char, and tar. The pyrolysis gas contains hydrogen, carbon monoxide, carbon dioxide, methane, and ethylene as its primary components. The composition ranges of each species is listed in Table 1. After scrubbing, the pyrolysis gas is compressed and sent to a liquefaction reactor. The liquefaction step, utilizing Fischer-Tropsch catalysts, produces the desired product: diesel type fuels. A schematic of the ASU process appears in Figure 1.

The work performed in this study focused on the continued development of a slurry phase Fischer-Tropsch reactor system for use in pyrolysis gas liquefaction. A characteristic of the Fischer-Tropsch reactions is their high exothermic heat of reaction. Removal of the heat of reaction is subsequently a primary consideration in the design of Fischer-Tropsch reactors. Slurry reactors provide excellent temperature control, and can operate at near isothermal conditions. They may be operated in a wider range of flowrates than a fluidized bed reactor, and are less prone to carbon fouling when carbon monoxide rich feeds are used.

Several models have been proposed for slurry Fischer-Tropsch reactors (14,34,49). Although the models themselves are quite general, a knowledge of the

Table 1. Composition of biomass derived pyrolysis gas (30).

Component	Mole Fraction
Hydrogen	.10 - .45
Methane	.10 - .45
Ethylene	.05 - .40
Ethane	.01 - .05
Carbon Monoxide	.15 - .60
Carbon Dioxide	0 - .15

Higher gaseous hydrocarbons are also present in small amounts.

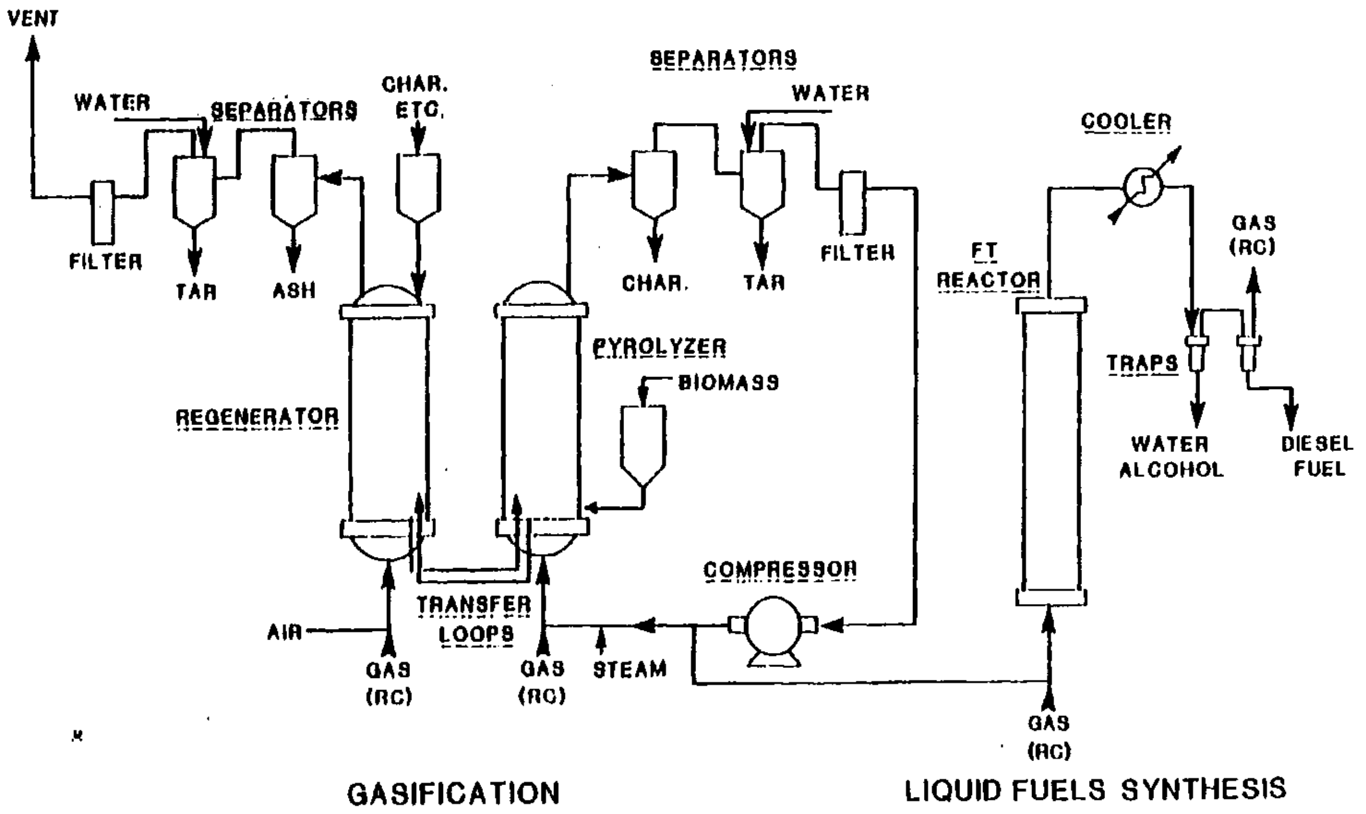

Figure 1. ASU biomass conversion process schematic.

reaction kinetics, heat and mass transfer coefficients, and hydrodynamics of the system are required. Reaction kinetics in particular are very specific to the catalyst used. The three models available are useful for predicting reactant conversions and cooling requirements; however, a method of predicting product distributions from reactant conversions is not available. Considering the unknown factors involved in modeling, it is not currently possible to predict a priori the performance of a slurry Fischer-Tropsch reactor. An experimental approach was consequently chosen to evaluate catalysts and liquids for use in the slurry reactor.

A variety of liquids have been tested as slurry liquids in previous studies at ASU (9,59). These liquids are listed in Table 2. The slurry liquid must be stable at elevated temperatures, and exert a low vapor pressure. Since some of the slurry liquid will undoubtedly be carried out of the reactor with the synthesis product, the slurry liquid must be compatible with the product. Part of this study was devoted to the testing of additional slurry liquids.

The most widely used catalysts in the Fischer-Tropsch synthesis are iron based. A previous investigation at ASU tested commercial iron based catalysts in

Table 2. Liquids tested previously for use in Fischer-Tropsch slurry reactors (9,59).

Commercial Diesel Fuel
Diethyl Phthalate
Dimethyl Naphthalene
Dow Corning 210H Fluid
Hexadecane
Mineral Motor Oil
Mobil-1 Synthetic Motor Oil
Paraffin Oil
1-Octadecene
Tetraethylene Glycol
Tetralin
Triethylene Glycol

a packed bed reactor (35). The performance of these catalysts was not encouraging. Nevertheless, there have been many reports in the literature on successful iron catalysts, and their preparation procedures are well documented in most cases. In light of the information available in the literature, additional iron catalyst testing was performed in this study, using catalysts designed specifically for use in the Fischer-Tropsch synthesis.

Using the best slurry liquid/best iron catalyst combination, a factor study and optimization was performed to determine the optimum set of operating conditions for producing the maximum liquid product yields. The factors considered were temperature, pressure, feed gas composition, and catalyst concentration in the slurry. The strategy followed in performing this work appears in Figure 2.

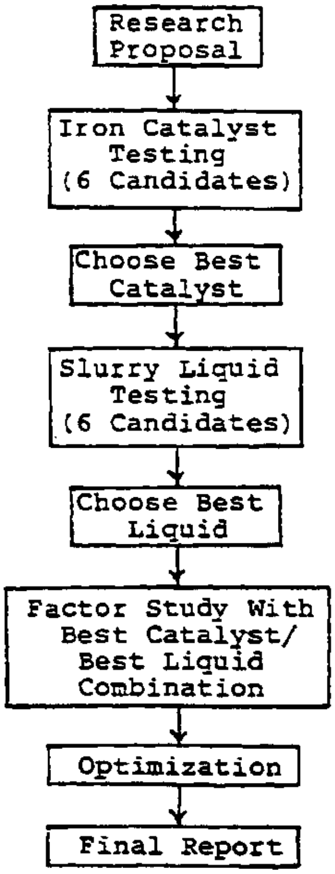

Figure 2. Strategy for research performed.

II. Review of the Fischer-Tropsch Synthesis

1. Historical Perspective.

Traditionally, the Fischer-Tropsch synthesis has been considered to be the catalytic formation of higher hydrocarbons via the hydrogenation of carbon monoxide. Sabatier and Senderens first reported the methanation of carbon monoxide over nickel and cobalt catalysts in 1902 (46). In 1913 and 1914, the Badische Analin und Soda Fabrik (BASF) received patents for the production of liquid, oxygenated hydrocarbons from carbon monoxide and hydrogen over a variety of metals, at pressures exceeding 100 atmospheres (3,4). Eventually, in 1926, Fischer and Tropsch were able to produce liquid hydrocarbons at atmospheric pressure by passing coal-derived synthesis gas over cobalt and iron catalysts (22).

A lack of petroleum reserves, an abundance of coal, harsh tariffs on imported fuel, and guaranteed prices for synthetic fuels encouraged the development of the German synthetic fuels industry, leading to the start up of the first commercial Fischer-Tropsch plant in 1936. By 1943, there were nine such plants operating in Germany, with a peak production capacity of 740,000 metric tons/year (16,29). The German technology