INVESTIGATING THE PRODUCTION AND USE OF TRANSPORTATION FUELS FROM INDIANA COALS

Rakesh Agrawal, Chemical Engineering
James M. Caruthers, Chemical Engineering
W. Nicholas Delgass, Chemical Engineering
Jay P. Gore, Mechanical Engineering
Robert D. Lucht, Mechanical Engineering
Fabio H. Ribeiro, Chemical Engineering
Thomas P. Seager, Civil Engineering
Wallace E. Tyner, Agricultural Economics
Yuan Zheng, Mechanical Engineering

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This is the final report for four groups involved in the investigation of the use of Indiana Coals for the production of transportation fuels. The report is divided in four sections covering the production, use, economics and environmental impact of fuels from coal.

A NOVEL PROCESS FOR THE PRODUCTION OF TRANSPORTATION FUELS

Rakesh Agrawal, W. Nicholas Delgass, Fabio H. Ribeiro
School of Chemical Engineering

Executive Summary

We propose a novel process to produce transportation fuels where coal is used as a source of carbon atoms and hydrogen, supplied from a carbon-free energy source, is added in the gasifier to produce synthesis gas[1, 2]. This process solves many of the problems with currently proposed solutions for synthetic fuel production. The carbon efficiency for this novel process is 100%, which is three times higher than the conventional process for coal transformation, leading to the release of the same amount of CO_2 as for petroleum usage. The key aspect of this new process is the ability to recycle CO_2 and add hydrogen into the gasifier.

Background and Significance of project

Dwindling oil supplies along with strong economic growth rate in developing countries have led to the recent sharp rise in crude oil prices. This rise is attracting the world's attention towards alternate sources for synthetic fuel production. The transformation of coal to liquid fuels comes to the forefront of such alternate processes. Countries rich in coal reserves are looking at coal-to-liquid processes as a means to wean their dependence on foreign oil. Although this process is feasible once the crude oil prices are above \$43/bbl[3], large inefficiencies in the coal-to-liquid (CTL) processes comes from conversion of coal to carbon dioxide in the coal gasifier and in the Fischer-Tropsch (FT) reactor. Due to this reason, more than two times the amount of carbon dioxide is generated for each unit of CTL fuels utilized as compared to fuel from crude oil. Generally, this carbon dioxide is released from the chemical processing system to the atmosphere and contributes to the green house gases in addition to the release of CO_2 from the exhaust of internal combustion engine. An alternative to produce liquid fuels which will minimize the release of carbon dioxide is thus a priority.

A frequently mentioned procedure to avoid release of CO_2 in the atmosphere during the coal conversion process is geologic carbon sequestration[4, 5]. Carbon capture at the source is done using amine absorbers and strippers. The captured carbon is stored in brine formations or in depleted oil or gas fields[4]. The control and monitoring of the captured CO_2 over geological time frames is a potential show-stopper[5]. In addition, this sequestered carbon dioxide would be a liability for millions of years to come. Also, CO_2 can only be captured from stationary sources like power plants.

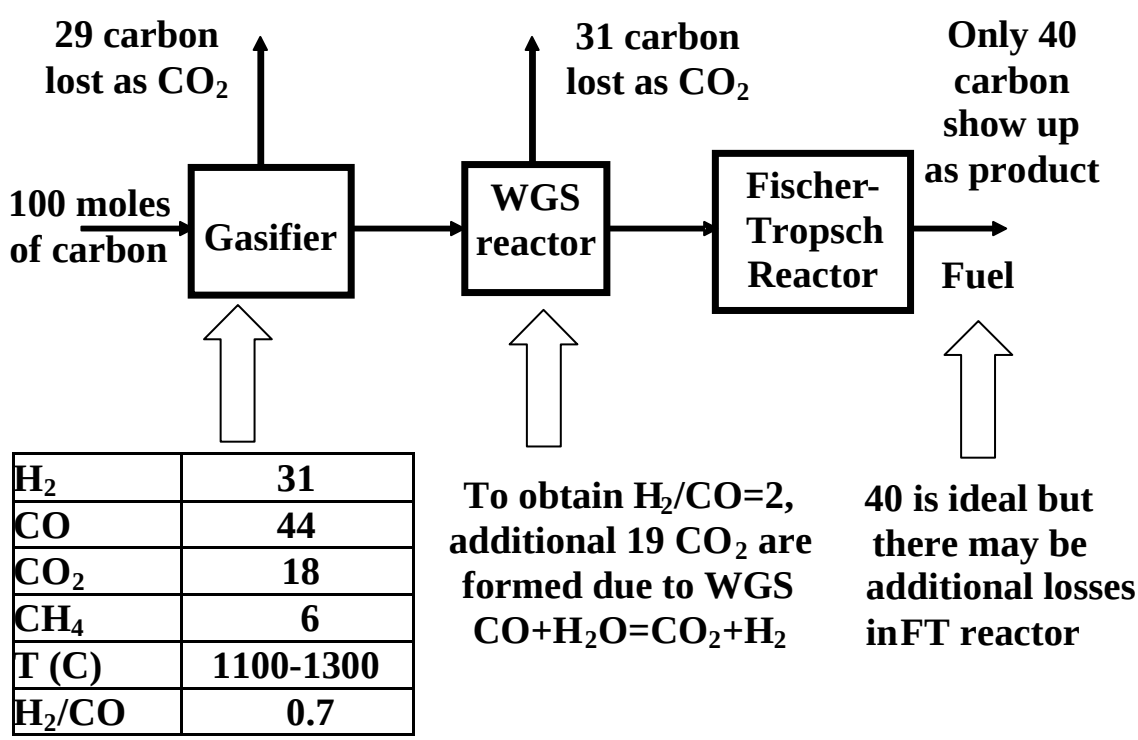
For the transportation sector, CO_2 capture is not viable. Therefore, alternate energy carriers like H_2 and battery powered vehicles have been proposed[6, 7]. A hydrogen economy has been cited as the perfect solution to the present growing energy crisis as well as a solution to greenhouse gas emissions from transportation fuels usage. Hydrogen has the potential to be derived from carbon-free energy sources but methods to store it in high volumetric density are not available. Hydrogen has very high energy content on a

mass basis compared to other fuels. However, transportation of fuels is limited by the volume of the vessels or diameter of pipe and hence, an accurate comparison can be only made on the basis of energy content per unit of volume[8]. On this basis, H_2 fares poorly in comparison to all other fuels because it is the lightest gas. Thus, even though H_2 can be generated at 60% efficiency, it can be delivered for end use only at 30% efficiency or less. Thus, a major challenge is the H_2 storage problem as a high density fuel.

Rechargeable battery powered vehicles are another option proposed to reduce greenhouse gas emissions. A major challenge involved with batteries is that the storage density of most commercial batteries is in the range of 75 to 150 Whr/kg[9] which is only sufficient for short distance driving.

Research Accomplishments to date

While reviewing coal to liquid fuels literature, we realized that a significant portion of the carbon atoms in coal is lost to the atmosphere during the conversion process, leading to a low liquid fuels yield and necessitating a need to sequester the CO_2 produced during the atmosphere. The reason for this low carbon conversion efficiency is the usage of energy content of coal to provide the energy for the process. This problem can be alleviated if the energy for the conversion process is derived from another carbon-free energy source. We depict the process of loss of carbon atoms in Figure 1 below.



H_2	31
CO	44
CO_2	18
CH_4	6
T (C)	1100-1300
H_2/CO	0.7

Data for Fluidized bed reactor from Steynberg and Dry, Fischer-Tropsch Technology,

Figure 1: Process of loss of carbon atoms in the conversion process

In order to overcome all the problems mentioned above, we recently proposed a novel process where coal is used as a source of carbon atoms and hydrogen supplied from a carbon-free energy source is used[1, 2]. Figure 2 shows a schematic of the process.

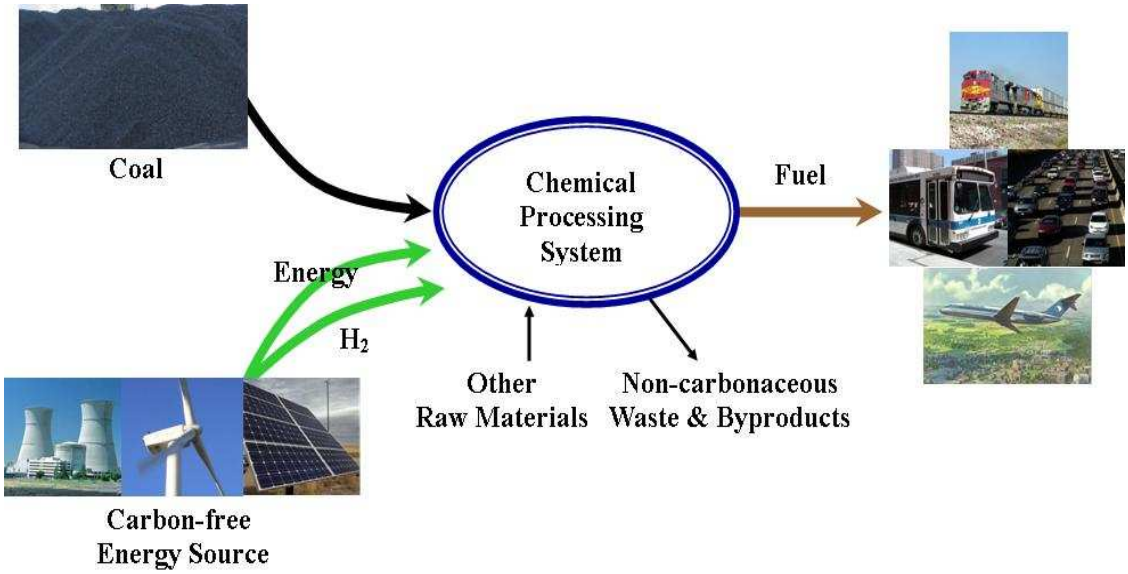


Figure 2: Schematic of Liquid hydrocarbon synthesis using coal and carbon-free energy source

There are a number of important implications of the proposed process

1. Coal is primarily a supplier of carbon atoms
2. H_2 is supplied from a carbon-free energy source such as solar and/or nuclear
3. The H_2 is used to convert every carbon atom to liquid fuel
4. No CO_2 is released during the liquid conversion process
5. It solves the H_2 storage problem of the so-called 'H_2-economy'

As a result, this process is a Hybrid <u>H_2</u>-<u>CAR</u>BON (H_2CAR®) route. The end results of H_2CAR® process are:

1. The carbon efficiency of the H_2CAR® process is three times higher than conventional process for the coal case
2. Coal will last for 144 years using H_2CAR® process instead of 89 years using conventional processes
3. The proposed process is overall much more energy efficient than the current conventional gasification route where no external source of H_2 is used
4. The proposed process releases only an amount of CO_2 equivalent to that for petroleum usage for the coal case.

To our knowledge, this is the first workable solution that can support the entire US transportation sector with a manageable land area using the current infrastructure.

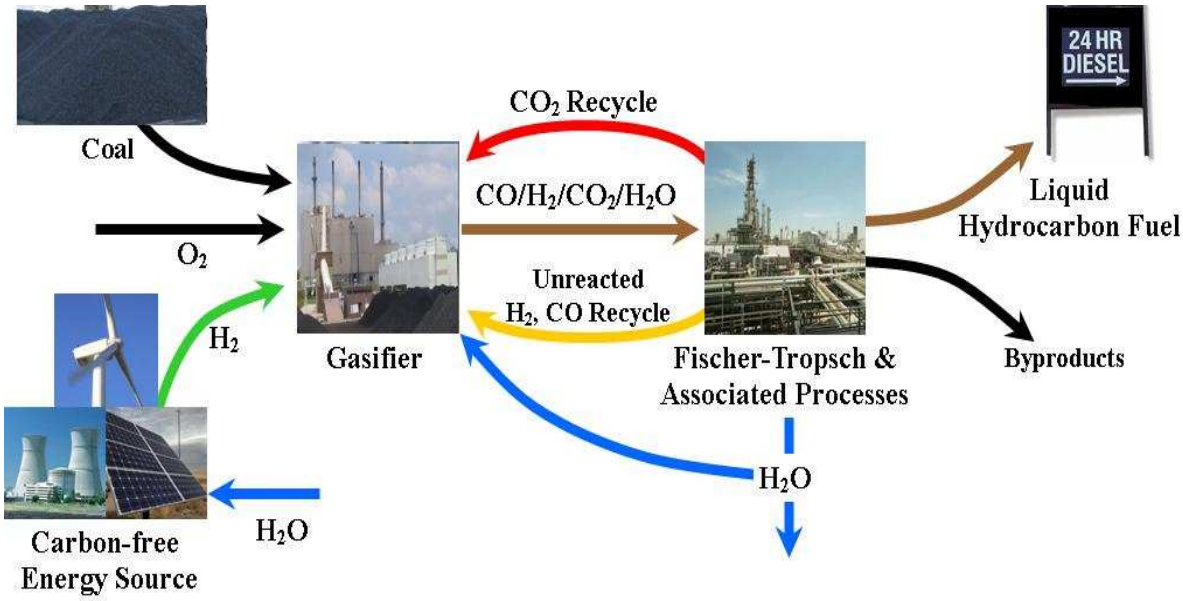


Figure 3: One of the many possible configurations of the $H_2CAR^{®}$ process

In order to quantify the novel configuration of the $H_2CAR^{®}$ process, the gasifier data reported in the NRC report[10] for the coal case was chosen. A schematic of the proposed process showing details of the chemical processing system is shown in figure 2. The novel aspects of the process are introduction of H_2 in the gasifier and recycle of unreacted CO, H_2 and all CO_2 to the gasifier. For our model calculations, we represent diesel as $C_{15}H_{32}$. The selectivity to the desired liquid molecule is taken as 100%. ASPEN Plus was used to simulate the current as well as the proposed process. Since actual composition of coal is not readily available along with all the desired properties required for running the ASPEN's RGibbs model, we used coal gasification data from the NRC report[10] and added H_2 from a carbon-free energy source and recycled CO_2 along with unreacted CO and H_2 to the gasifier. This is equivalent to the recycling of H_2 and CO_2 in the conventional gasifier just before the exit of syngas from the gasifier. This is allowed because the gasifier is at thermodynamic equilibrium so, no matter where H_2, recycled CO_2 and unreacted CO and H_2 is fed, the exhaust composition will be the same because the equilibrium composition depends only on the operating temperature and pressure of the gasifier.

With the above-mentioned configurations, there will be a carbon efficiency increase by a factor of three for coal cases. For the coal to liquids, $H_2CAR^{®}$ process avoids sequestration of 0.9 GtC/yr. In addition, H_2 requirement for $H_2CAR^{®}$ process is nearly the same for that required for H_2 fuel cell vehicles but storage of H_2 as liquid hydrocarbon fuel eliminates the need for a new infrastructure. Additionally, longevity of coal increases significantly. At current consumption rate of 1.13 billion tons/yr, US coal will last for 244 yrs. With Additional production of 13.8 Mbbl/d of oil using conventional process, life time of coal decreases to 89 yrs. Using $H_2CAR^{®}$, coal can last for 144 yrs.

Planned Future Work

Task 1: Once this validation is done, demonstration of the novel gasifier configuration is needed. This demonstration will involve co-feeding of H_2 and CO_2 in the gasifier along with coal, O_2 and steam. Effect of the following parameters on the exiting syngas from the novel gasifier needs to studied:

1. Temperature
2. Pressure
3. Amount of CO_2 fed
4. Amount of H_2 fed

Task 2: Kinetic data will be gathered for this novel configuration so that it can be modeled.

Task 3: Once the kinetic data is available, modeling of this gasifier is required. Modeling of the novel gasifier will provide many insights that are not easily accessible using experiments.

Task 4: For the feasibility calculations using ASPEN Plus, we assumed that a single type molecule ($C_{15}H_{32}$) is formed from the Fischer-Tropsch reactor. However, in reality the FT catalysts give a distribution of products and the longer chain molecules must be hydro-cracked to diesel range molecules. There is a need to find an ideal chain growth probability value for the H_2CAR process which will maximize diesel production.

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A **PRELIMINARY STUDY OF SURROGATES FOR FISCHER-TROPSCH JET FUELS**

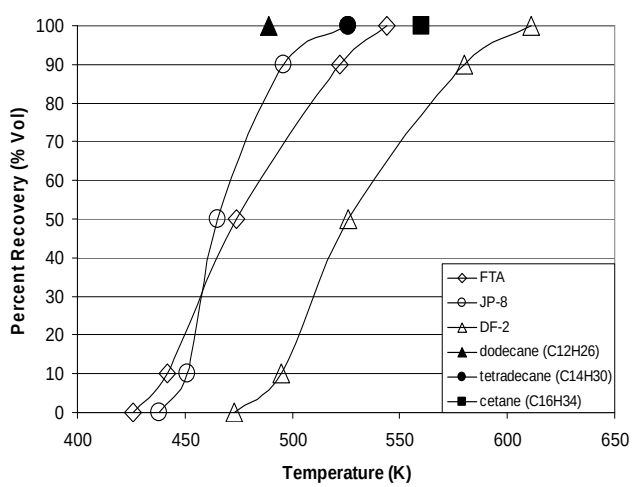
Robert Lucht, Jay Gore, Yuan Zheng
School of Mechanical Engineering

A proposal including research needs for Fischer-Tropsch (FT) jet fuels had been submitted to CCTR last August (Ribeiro, et al., 2006, Investigating the Production and Use of Transportation Fuels from Indiana Coals). One of the major research needs described in that report is to select appropriate surrogate mixtures for FT jet fuel. The compositions of commercial FT jet fuels are very complicated. FT fuels consist of approximately 90% iso-paraffins and 10% n-paraffins, mainly in the C8 to C17 range, with an average carbon number around 13 and H/C ratio near 2.1. To understand the effects of the fuel components on combustion and emission under aviation gas turbine conditions, surrogate mixtures that are commercially available at reasonable cost should be selected. Since last summer, we have conducted a preliminary investigation to select surrogate or surrogate mixtures to represent physical and/or chemical characteristics of FT jet fuels.

Physical Surrogate

Physical surrogate is a mixture of pure fuels that has generally same physical properties as the FT jet fuel. Physical properties, such as density, viscosity, etc., have effects on fuel spray and eventually on gas turbine design and modification.

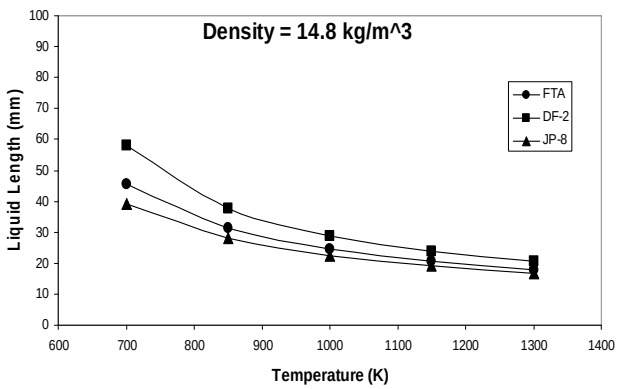
Fuel spray characteristics, such as droplet life time and liquid fuel length (fuel penetration), may be determined by the 90% distillation temperature (T90) of the fuel (Siebers, 1998, SAE paper 980809). By comparing T90 of the commercial fuel to the boiling point of a single component fuel, the surrogate for spray study can be selected.



According to the above figure, we found that dodecane ($C_{12}H_{26}$), tetradecane ($C_{14}H_{30}$) and cetane ($C_{16}H_{34}$) are good surrogates for JP-8, a specific FT fuel (FTA) and No. 2 Diesel (DF-2) respectively. After choosing the surrogates, the different spray behaviors of these three fuels can be investigated under combustor conditions.

With same ambient condition (1000 K, 40 bar) and nozzle diameter (0.5 mm), the droplet life times of JP-8, FTA and DF-2 are 0.72s, 0.77s and 0.86s respectively.

The liquid length of these three fuels also changes under the same combustor design as illustrated by the following figure. With a same condition, the liquid length becomes longer from JP-8 to FTA to DF-2. This difference is significant at lower temperature and pressure but becomes not appreciable at higher temperature and pressure. (The ambient density keeps the same).



The effect of these spray characteristics on final gas turbine combustor design needs to be further investigated. Also, a very helpful tool in selecting physical surrogates developed by the National Institute of Standards and Technology, NIST Thermophysical Properties of Hydrocarbon Mixtures Database: Version 3.1, may be purchased to facilitate future investigations.

Chemical Surrogate

Chemical surrogate is a mixture of pure fuels that has generally same chemical properties, for example combustion properties, as the FT jet fuel. Soot emission may be dependent on some trace species therefore more consideration in choosing surrogate is desired.

A surrogate mixture of 14 pure hydrocarbon fuels was used to represent JP-4 (Wood, et al., 1989, Journal of Propulsion, 5, 399-405). This surrogate followed the distillation curve and compound class composition of JP-4 except having a much higher smoke point. In the experimental tests, the mean droplet velocity and Sauter mean diameter profiles and mean temperature contours of the surrogate and the parent fuel matched very well.

Detailed FT fuel combustion chemistry is critical to combustion efficiency and pollutant formation. To validate the surrogate combustion/emission properties, laminar premixed flame structure data, including major and intermediate species profiles and temperature profiles can be very informative (Doute, et al., 1995, Combustion Science and Technology, 106, 327-344). In addition, in order to implement "fuel tuning" task of this overall coal to liquid transportation fuel project, the effects on combustion and emission of single component of the FT fuels can be first investigated through this kind of flame structure studies. Gas chromatographer with high order hydrocarbon capability and advanced laser-based temperature diagnostics are desired for this investigation.

Near Future Work

In the near future, we may make an FT fuel surrogate using one iso-paraffin (90%) and one n-paraffin (10%) as the first approximation. This surrogate should follow the distillation curve of a FT fuel and has similar smoking point, flame velocity and ignition delay to the parent fuel.

We can further validate this surrogate through spray and combustion tests using facilities available at Zucrow and/or ME laboratories. Spray drop size distribution, spray patternation and laminar premixed flame structure will be measured and compared to the measurements of the parent FT fuel and JP-8.

This study will facilitate fuel/air mixing investigation, tests in subscale gas turbine combustors and the fuel tuning study in the long term.

ECONOMIC ANALYSIS OF COAL LIQUIDS POLICY OPTIONS

Wallace E. Tyner
Department of Agricultural Economics

Our economic analysis is based on coal to liquids plant cost information contained in the Southern States Energy Board report, *American Energy Security: Building a Bridge to Energy Independence and to a Sustainable Energy Future*, released in July 2006. We used case number five, a 60,000 barrel per day plant with sequestration of CO_2. The total capital cost of the plant is $3.9 billion. Following the case authors, we assumed one third equity and two-thirds debt financing. The debt interest rate is 8 percent and the required minimum return on equity is 15 percent. The assumed inflation rate was 3 percent. We used other economic assumptions provided by the study authors (Table 1). We calculated a break-even price of $43/bbl. crude oil equivalent, close to the $44 obtained by the authors.

Table 1: Economic Assumptions for the Coal Liquids Policy Analysis

Economic Parameter / Assumption		**Value**
Construction Period		3 years
Year 1Incurred Capital Cost Construction		20%
Year 2 Incurred Capital Cost Construction		50%
Year 3 Incurred Capital Cost Construction		30%
1st Year Availability		45%
2nd Year Availability		81%
3rd Year and Beyond Availability		90%
Plant Lifetime	years	25 years
Return on Equity		15%
Depreciation Method		DDB-16 yrs.
Debt:Equity Ratio		2/1
Interest Rate		8%
Inflation Rate		3%
Tax Rate		36%
Electricity Selling Price	$ / MWhr	$35.60
Sulfur Price	$ per ton	$80
Bituminous Coal Price	$ per ton	$36
Subbituminous Coal Price	$ per ton	$11
Lignite Price	$ per ton	$10
Woody Biomass Price	$ per ton dry	$20
Naphtha Value	times diesel value	$0.714

We then introduced stochastics into the analysis, thus far in the form of capital cost uncertainty and oil price uncertainty. Capital cost uncertainty was modeled as a simple triangular distribution. However, oil price was much more complex. We calculated the mean and standard deviation of real annual oil price change over the past 25 years. Twenty five years was chosen because the prices changes were much lower in earlier years. The mean price change was very close to zero, and the standard deviation was $9.20 per year. We constrained annual price changes to plus or minus $23 per year, the largest experienced in the past 25 years. Future price scenarios were then simulated with a constraint that the future price could not fall below $15 (2006$), the lowest price in the past 25 years nor higher than $200, chosen arbitrarily.[1] Under these conditions, we simulated a series of future prices with base prices ranging from $40 to $70. All of this uncertainty was captured in a Monte Carlo simulation using @Risk software and doing 10,000 iterations for each simulation.

Outputs included net present value of the project, internal rate of return, chance of a loss, and present value and annualized value of the sum of diesel and naptha sales. For each of these outputs, we have the mean (expected value), standard deviation, and all elements of the probability distribution.

The simulations to date have been done for the base case and the policy of a variable subsidy. We tested different levels of the variable subsidy with it kicking in at $35, $40, and $45. That is, there is no subsidy if crude oil average annual price is above the stipulated level, but a variable subsidy equal to the difference between the market price and the stipulated level if the market price is below the subsidy floor. For example, if market price were $40 and the price floor $45, there would be a subsidy of $5 per barrel of crude oil equivalent fuel produced. If the market price is above $45, there is no subsidy. The actual subsidies were converted to diesel using a historic regression relation between crude oil prices and diesel prices.

The key output values are chance of a loss for each price and policy simulation and government cost for each policy alternative. Figure 1 illustrates the probability of a loss for each base price case and for the $45 price floor policy alternative. The interpretation of the graph is as follows. The first number in the number pairs is the base price, and the second is the price floor. For this graph, the price floor is always $45. One can see that if the base price is $40, the chance of a loss with no policy intervention is greater than 50 percent. If the base price is $70, then the probability of a loss is around 10 percent. One can think of the base prices as the central tendency, that is the price around which future prices are expected to move. Just barely visible along the X axis, one can see that the chance of a loss with a $45 price floor subsidy is always zero, regardless of the base price. So clearly, a $45 price floor policy is quite effective at reducing risk and thereby stimulating investment in coal liquids.

Another question is how much would this subsidy cost the government. The answer, of course, depends on what future crude oil prices do. Figure 2 displays the expected government cost for each of the base prices. These costs are expressed in terms of $/gal. of diesel produced. They were calculated as the difference between the diesel

[1] The results were not very sensitive to the level of this upper limit.

sales revenue with and without the policy in effect. The expected costs range from 11 cents per gallon with a $70 base price to 40 cents per gallon with a $40 base price. Any of these costs are less than most estimates of the national security cost of imported oil. Also, of course, if the crude oil price were to remain above $45 for the 25 year life of the plant, the government cost would be zero.

In the future with additional funding, we intend to apply this general approach described to other policy options and to examine other ways of incorporating future price uncertainty. We will also add uncertainty in other variables such as coal cost.

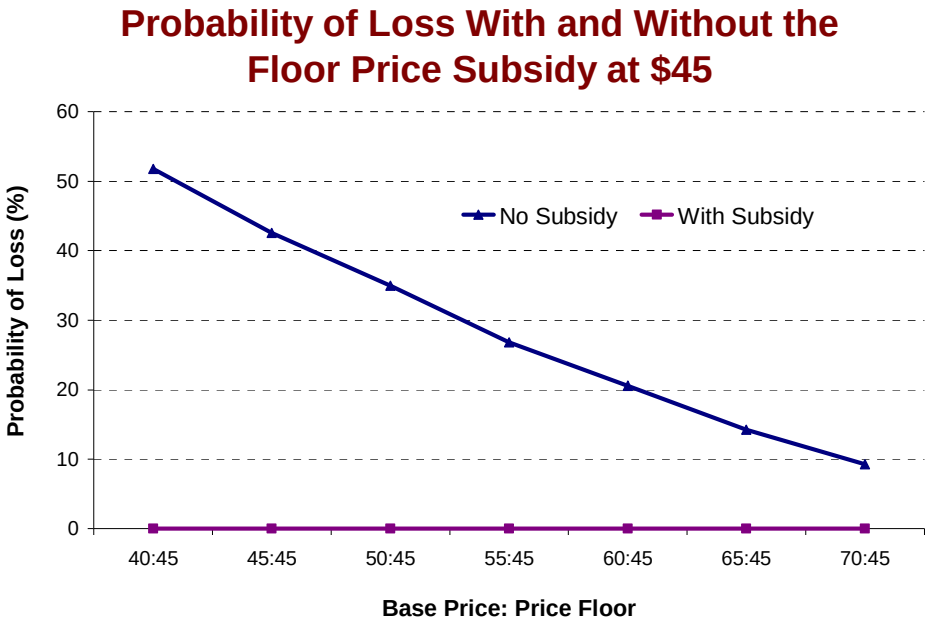


Figure 1

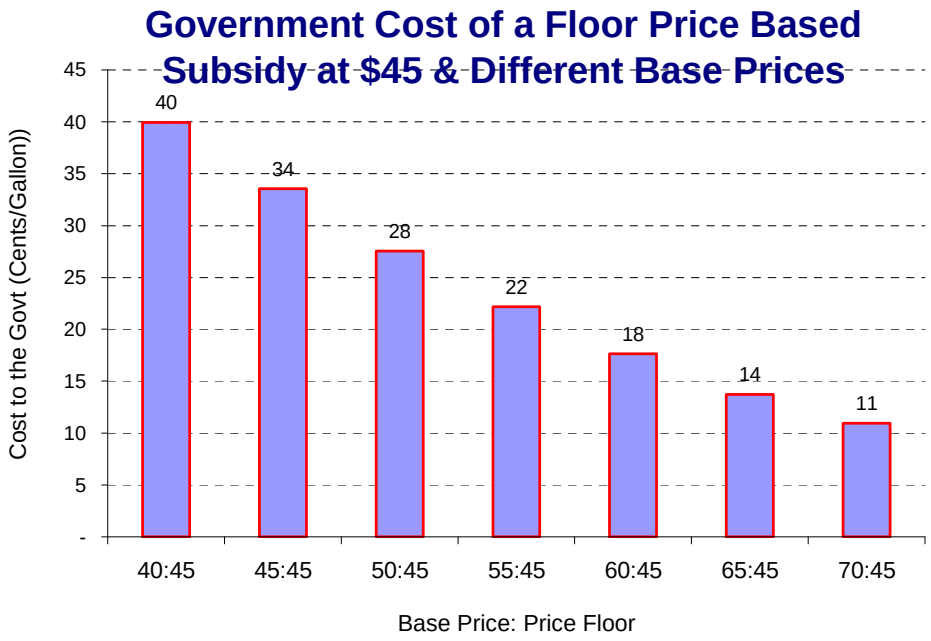


Figure 2

SUMMARY OF F/T ENVIRONMENTAL TEAM RESEARCH

Thomas P. Seager
Civil Engineering

The environmental research with regard to Fischer-Tropsch fuel production has focused on identifying the waste and byproducts generated in the F/T fuel life cycle and developing technologies for environmentally responsible, economically viable beneficial reuse of these materials. This research is motivated by the hypothesis that beneficial reuse of waste products will reduce both economic and environmental barriers to F/T technology deployment, including production and regulatory compliance costs. Our first task has been to create a mass-balance model of the F/T production process and identify critical components of the coal that are not incorporated in the final fuel product but may be viable for reuse. The second task has been to investigate the potential beneficial reuse of coal fly ash in alternative building materials such as geopolymer concrete products.

The life-cycle modeling project has resulted in a model F/T process flow chart showing material flows, recycle paths, environmental treatment processes and final product and waste outputs. Our current efforts are focused on characterization of Illinois basin coals for the purpose of predicting waste outputs as a function of the composition of the coal. This information will be critically important to design beneficial reuse strategies that are suitable for the coals available. Future research is expected to focus on development of a quantitative material and energy flow model tracking essential coal components through the F/T fuel production process for the purpose of predicting waste volumes and compositions. The key challenge in creating this model is integrating the many different unit processes such as coal preparation, gasification, syngas purification, F/T synthesis and refining into a single model. The model output will be a catalogue of input demands (e.g., coal, water, catalyst, electricity) and process outputs (e.g., ash, sulfur, naptha, wastewater) that will facilitate development of beneficial reuse technologies.

One of the critically important by-products of F/T production is expected to be ash. Currently, some Class C coal fly ash is currently recycled in the building construction industry as a substitute for ordinary portland cement (OPC), thereby reducing the cost and environmental burden of OPC concretes. However, class F and N fly ashes are not suitable for this purpose. The second aspect of the environmental research investigates the potential to reuse class F or N ashes in an alternative alumino-silicate concrete called geopolymer. When produced under laboratory conditions, geopolymer concretes exhibit superior strength gain, durability and life-cycle environmental properties. However, it is considerably more challenging to batch geopolymer concrete from real ash than from laboratory-grade materials. Moreover, the potential environmental leaching properties of coal ash-based geopolymers have not been investigated. This project has developed an experimental approach to investigation of the environmental suitability of geopolymers in comparison to OPC. The next step will be to develop a generic formula for batching geopolymer concretes from a variety of ash types and testing the structural integrity of coal-ash based building materials such as geopolymer bricks, pavers, masonry units, pipes, tanks or steel-reinforced geopolymer structures to determine the viability of co-locating building product manufacturing facilities with F/T production facilities.