Novel Methods for Converting Coal and Biomass to Liquid Fuel

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INTRODUCTION

In order to meet the demand of the Energy Independence and Security Act of 2007 (EISA), a requirement of 36 billion gallons of renewable fuels by 2022, many different sources of biofuels must be considered. However despite the advances in growth and conversion of switchgrass (David, 2010), algae (Demibras, 2008), and other feedstocks currently used for liquid fuels, there still remains a gap in replacing enough foreign oil to make a major impact on energy independence. The U.S. presently imports about 58% of the crude oil that is used to generate most of the 180 billion gallons of gasoline and diesel that are consumed in this country on an annual basis (EERE, 2007). The importation of these vast quantities of fossil fuels is fraught with many dangers, including

- Economic reasons—*the price of crude oil is controlled by others, and the importation of vast quantities of crude significantly upsets our balance of payments*
- Security reasons—*much of the crude oil comes from areas that are less than friendly toward the U.S.*
- Environmental reasons—*the continued build up of* CO_2 *in the atmosphere contributes greatly to global warming*

The use of U.S. grown, carbon-neutral lignocellulosic biomass as a liquid fuel source can help to alleviate these problems, both as a permanent solution and as a bridge to alternative energy technologies. It is estimated that there are at least 500 million dry tons of biomass available in the U.S. annually in the form of forest residues, mill residues, potential dedicated energy crops, urban wood waste, and agricultural residues (Bain *et al.*, 2003). Using a conservative conversion efficiency of 50 gallons of liquid fuel per dry ton, *over 25 billion gallons of liquid fuel could be generated from biomass feedstocks, or 14% of our liquid fuel needs*. By contrast, the U.S. produced a record 13.2 billion gallons of ethanol from corn in 2010 (EERE News, 2011), accounting for less than 3% of our liquid fuel needs. Obviously, the conversion of lignocellulosic and other biomass to liquid fuel will drastically decrease the U.S. dependence on foreign oil. However, even with conversion of lignocellulosics to liquid fuel products, the amount of biofuel from biomass is still low. In order to truly reach energy independence in the United

States, non-biomass feedstocks must also be utilized in producing liquid fuels. Even though the US has hundreds of years of coal (Schobert, 2002), severe technical and economic challenges remain in the conversion of this coal to transport fuel (McKendry, 2002). Furthermore, the use of biomass/coal blends to produce liquid fuels has received little attention. However, we have determined that coal, often gasified at 1500 C, produces a significant amount of waste heat for biomass pyrolysis, often carried out at 500 C, and thus a linear process is postulated where waste heat from the coal is used to turn the biomass into liquid fuels. Advantages of the proposed process (ie, Arkansas) include:

- The thermal efficiency of the gasifier will be significantly increased over the ~40% efficiency reported in current systems by using waste heat from coal gasification for biomass pyrolysis.
- Biomass pyrolysis will produce liquid intermediates rather forming synthesis gas. This will save energy that would be required later in the process.
- Hydrotreating will be carried using Isotherming^{TM} patented technology from Process Dynamics, allowing for a significant decrease in capital and operating costs.
- Catalyst and optimum temperature design in Fisher Tropsch and hydrotreating will allow for maximum liquid product yield.
- The system will be designed for an optimum coal:biomass ratio utilizing all of the waste heat from coal gasification for biomass pyrolysis. This will permit maximum conversion of energy to liquid fuels.

Thus, the objectives of this proposal are to:

- *Test the concept of using waste heat from coal gasification for biomass pyrolysis*
- *Determine optimum coal/biomass ratios for maximum thermal efficiency*
- *Determine the possibility of recycling biochar from biomass pyrolysis back to the gasifier*
- *Use Fisher Tropsch synthesis to convert synthesis gas (syngas) into liquid fuel and hydrotreating to convert bio-oils into liquid fuels*

- *Show by life cycle assessment and energy balance that this process has favorable energy and carbon balances*

The following background sections will review pertinent research that has been done in: coal gasification, biomass pyrolysis, Fisher Tropsch, hydrotreating, and life cycle and economic assessment of these processes.

BACKGROUND

Coal Gasification

When considering energy independence in the U.S., coal is an excellent feedstock because of the total reserves available. According to Miller (2005), the U.S. has the largest recoverable coal reserves in the world at 273.6 billion short tons as compared to second-place Russia at 173.1 billion short tons. U.S. coal is predominantly used in power production, and direct conversion to liquid fuels remains a challenge. Coal gasification is a difficult process due to high gasification temperatures and low thermal efficiencies obtained. Gasification was first proposed by Farben in the 1930's and nearly a dozen plants were built by the end of World War II for the production of liquid fuels (Wu and Storch, 1968). Although this technology has existed for over 80 years, conversion, energy recovery, and cheap oil from the Middle East have plagued further development. Several processes have been proposed for gasification which are outlined in Table 1 (Higman, 2008). As shown in the table,

Table 1: Characteristics of Different Categories of Gasification Process

Category	**Moving Bed**		**Fluid Bed**		**Entrained Flow**
Ash conditions	**Dry ash**	**Slagging**	**Dry ash**	**Agglomerating**	**Slagging**
Typical processes	Lurgi	BGL	Winkler, HTW, CFB	KRW, U-Gas	Shell, Texaco, E-Gas, Noell, KT
Feed characteristics					
Size	6-50 mm	6-50 mm	6-10 mm	6-10 mm	<100 µm
Acceptability of fines	Limited	Better than dry ash	Good	Better	Unlimited
Acceptability of caking coal	Yes (with stirrer)	Yes	Possibility	Yes	Yes
Preferred coal rank	Any	High	Low	Any	Any
Operating characteristics					

Outlet gas temperature	Low (425-650°C)	Low (425-650°C)	Moderate (900-1050°C)	Moderate (900-1050°C)	High (1250-1600°C)
Oxidant demand	Low	Low	Moderate	Moderate	High
Steam demand	High	Low	Moderate	Moderate	Low
Other characteristics	Hydrocarbons in gas	Hydrocarbons in gas	Lower carbon conversion	Lower carbon conversion	Pure gas, high carbon conversion

entrained flow slagging type gasifiers have the highest carbon conversion but also run at temperatures (1250-1600 C) that are very difficult to obtain in conventional reactors. On the other end of the scale, the Lurgi process requires much lower temperatures (425-600 C) but has a high steam demand and still gives hydrocarbons in the gas stream and a much lower conversion. A general discussion of these basic techniques is given below.

Entrained flow high temperature gasification

Many different high temperature processes have been developed including the Shell, Texaco, E-Gas, Noell, and KT. In terms of pure chemical equilibrium, all of these processes are similar (the input and the output are about the same), but in practice, the way that the heat is introduced, the feed is prepared, etc are different. Zheng and Furinsky (2005) did Aspen simulations of many of the different gasifier designs and found the thermal efficiency varied from 39% to 43% for multiple coals across multiple gasifiers. The high temperatures and pressures required in these gasifiers are based on equilibrium conversion. For instance, Higman (2008) found that at 1000 C and 30 bar a process would yield 50% CO and 5 % CO_2, while raising the temperature to 1500 C gave 62% CO and <1% CO_2. This >20% increase in the carbon efficiency to synthesis gas is often worth the extra expense of heating an additional 500 C. Conversely, Higman (2008) found that at 1000 C, pressure had the opposite effect: operation at atmospheric pressure gave 60% CO and <1% CO_2 while operation at 100 bar gave 39% CO and 10% CO_2. Thus, there is a sweet spot of high temperature gasification that leads to smaller reactors, optimum product yield, and efficient thermal exchange.

Of the several different processes proposed for coal gasification, the Texaco process (later purchased by GE Energy) is probably the most widely used. Two demonstration units were put in place in the late 1970s and three commercial scale facilities were started between 1983 and 1985 (Curran and

Tyree, 1998). Since 1990, 9 commercial units (5 in the US, 4 in China) have been built for producing electricity (Higman, 2008). In this process coal slurry is wet-milled to a particle size of about 100 μm. A pressure of up to 30-80 bar is used, depending on the application, and the temperature is typically 1425 C. At these conditions, the reaction only takes 0.5 – 4 seconds (Higman, 2008). In the quench configuration, hot syngas leaves the reactor at the bottom with molten slag. After cooling to approximately 760 C by total quench, molten slag solidifies and is removed in a lock-hopper arrangement. Finally, in a radiant cooling concept, the temperature is reduced to about 425 C if electricity is to be produced or other temperatures for other applications. The Texaco process is the most economical design on the market, but can require a standby reactor because it is maintenance intensive (Moock and Trapp, 2002). *However, the ease of the design and the low capital investment make this reactor design a perfect match for integrated coal and biomass production. Thus, the gasifier in this proposed work is based on the Texaco design.*

Many other high temperature gasifiers exist in the marketplace. The E-Gas gasifier is a two-stage coal-water slurry slagging gasifier. The second stage is typically operated at a lower temperature (Liu et al, 2010) and so slagging only occurs in the high temperature part of the process. Further, the heat can be integrated from the high temperature to the low temperature stage potentially increasing thermal efficiency. Although this design is more expensive, it is the only commercial process that does not require a lock hopper for slag removal (Higman and van der Burgt, 2008). The Shell process has only been demonstrated with dry feed at slagging temperatures and has the advantage of allowing for syngas and slag to be separated in the reactor itself. It is also the only process to use a membrane wall for partial separation of the gases.

Fluidized and Moving Bed Gasifier

A fluid bed gasifier has excellent mixing between the fuel and oxidant, promoting heat and mass transfer. Since the temperatures are generally kept below the softening point of ash, the time required in the reactor is longer than that in the entrained flow reactors. At lower operating temperatures (1050 C) and moderate pressure (30 bar), Adlhoch et al. (1990 and 1991) obtained 28% CO, 28% H_2, and 17% CO_2. Further, Kunii and Levenspiel (1991) found that the ash in fluidized beds contained almost 20% of the carbon. Thus, although the energy efficiency is better for fluidized beds, the carbon conversion is much lower. Demonstrations have been made of various moving bed processes include demonstrations of the Winkler process with 70+ reactors (Bogner and Wintrup, 1984), the HRL process (Anon, 2007), the KBR (Smith et al., 2002), and U-Gas technology (Vail, 2007).

A moving bed (or fixed bed) gasifier moves the coal countercurrently against hot synthesis gas. The temperature is even lower in this process (425 - 600 C) which gives better thermal efficiency; however, the final product is very low grade. Sharma et al. (2008) found that for several single and two stage processes running in the moving bed configuration, the composition of the final product was 5-19% hydrocarbon gases, 14-65% light oils (C5), 10-33% middle oil, and 7-48% unreacted coal. However, despite these difficulties, the Lurgi moving bed process is still the most widely used coal gasifier technology in the world (Higman, 2008). Despite the thermal efficiency advantages of moving beds and fluidized beds, we have chosen a fixed bed high temperature approach in our process *since we are attempting to increase the thermal efficiency of this high temperature process by using the waste heat to upgrade biomass.*

Biomass Pyrolysis

Fast pyrolysis is the most common thermal process for direct liquefaction of biomass to bio-oil or bio-crude. Fast pyrolysis is characterized by reaction temperatures of about 500°C, short residence times of <2 sec and rapid cooling of vapors (Bridgwater, 2006). The resulting bio-oil is a mixture of more than 100 chemical species with a wide range of molecular weights (Evans and Milne, 1987). The oil is rather viscous (30-200 cp) and has a medium heating value (17 MJ/kg, as produced). It has high water content and, just like the biomass feedstock, is highly oxygenated. A typical elemental composition shows 44-47% carbon, 6-7% hydrogen, 46-48% oxygen and 0-0.2% nitrogen (Bridgwater *et al*., 1999). Bio-oil is a suitable fuel for boilers, automobile and truck engines, and turbines or diesel engines to produce electricity (Bridgwater, 2006). However, because of the high water content and the presence of oxygenated compounds, the heating value of bio-oil is only 50% of the heating value of diesel fuel (Briens *et al*., 2008), which limits its use.

A number of reactor types have been developed for the fast pyrolysis of biomass including fluidized bed and ablative reactors. However, only the fluidized beds are used commercially at this time (Abou-Zaid and Scott, 2012). Examples of reactors for fast pyrolysis include the bubbling fluid bed, the circulating fluid bed, the rotating cone and the twin screw (Henrich and Weirich, 2004). All fluidized beds use a solid heat carrier, such as sand, to ensure a fast heat transfer rate. Typical conversions of biomass to oil are about 75%.

There are a number of problems associated with the fast pyrolysis of biomass as presently practiced:

- The biomass feedstock must be dried to a moisture content of <10%, and ground to a particle size of <2 mm to ensure rapid reaction (Briens *et al.*, 2008). Biomass pretreatment prior to liquefaction can be expensive unless waste heat is utilized.
- Difficult to handle sand or other solid carrier is required in the fluidized bed to reach and maintain the required temperature of 500°C and ensure a fast heat transfer rate (Agrawal and Singh, 2009), conditions that are essential for efficient fast pyrolysis.
- The bio-oil resulting from traditional fast pyrolysis has limited use as a petroleum product, which necessitates upgrading by hydrodeoxygenation (HDO) using H_2 in the presence of a catalyst (Huber et al., 2006; Elliott, 2007; Elliott and Neuenschwander, 1996). A convenient and inexpensive source of H_2 is thus required.

This proposal addresses each of these problems by using a feedstock consisting of coal and biomass. Coal is gasified at about 1500°C to produce a syngas that is rich in H_2*, while also containing* CO*,* CO_2 *and* H_2O*. The hot gas may be used in heating the biomass, thus eliminating the need for cumbersome sand in the pyrolysis reactor. Significant quantities of waste heat are available in the syngas to pretreat the biomass by reducing its moisture content. The* H_2 *in the syngas is available for bio-oil upgrading (during bio-oil production) by hydrodeoxygenation, although it is likely that separation of the* H_2 *from the syngas will be needed prior to its introduction. Finally, char from fast pyrolysis is available for recycle to the gasifier.*

Table 2 presents a comparison of the carbon efficiencies, process energy efficiencies and liquid fuel yields for various biofuel technologies from Agrawal and Singh (2009). Traditional fast pyrolysis has a carbon efficiency of almost 70%, far above the carbon efficiencies of cellulosic ethanol or gasification/Fisher Tropsch processes. In addition, the process energy efficiency of fast pyrolysis is 77% and the liquid fuel yield in gallons of ethanol equivalents per ton of biomass is 163 gal/ton (once again, significantly above the carbon efficiencies of cellulosic ethanol or gasification/Fisher Tropsch processes). If hydrodeoxygenation is coupled to fast pyrolysis (called fast hydropyrolysis and hydrodeoxygenation), the process energy efficiency potentially rises to 82% and the liquid fuel yield rises to 230 gal/ton.

Table 2. Comparison of Liquid Fuel Yields from Various Biofuel Technologies

(from Agrawal and Singh, 2009)

Biofuel Technology	Carbon Efficiency (%)	Process Energy Efficiency (%)	Liquid Fuel Yield (Ethanol Gallon Equivalent/ton Biomass)
Cellulosic ethanol	36.8	35-57	74-121
Biomass gasification/Fisher Tropsch	36.7	40.6	86
Biomass fast pyrolysis	69.7	77	163
Biomass fast hydropyrolysis and hydrodeoxygenation*	69.7	81.7	230

*hydrogen supplied from methane reforming or coal gasification

Fisher Tropsch

Fisher Tropsch syntheses utilize reactions that are designed to react CO and H_2 (from synthesis gas) into desirable hydrocarbons. The process is typically operated at a temperature of 150-300 C and uses a catalyst to aid the reaction. An important process used with Fisher Tropsch is the water gas shift reaction, which adjusts the H_2/CO ratio to enable the production of certain liquid products. This comes with a price, however, since some CO is also converted to CO_2, an undesired by-product. When comparing feedstocks for Fisher Tropsch syntheses, the ratios of H_2/CO/CO_2 mole % were 35:52:11, 39:19:30, and 29:30:28 for high temperature gasification of coal, low temperature (moving bed) gasification of coal, and the gasification of woody biomass, respectively (Vander, 1999; Logdberg, 2007). Thus, even though the moving bed gasification of coal is generally recognized for giving the optimum syngas ratio for upgrading to biofuels, a significant amount of carbon is converted to the undesirable by-product CO_2. Thus, a water gas shift can be performed with high temperature gasification to increase the overall carbon efficiency. Reichling and Kulacki (2011) performed a review of several different coal and biomass feedstocks and found that the overall thermal efficiency ranged from a low of 43.6% for biomass as a feedstock (Tijmensen et al., 2002) to a high of 60.5% with coal as a feedstock (Yamashita and Barretto, 2003). Their study concluded that, for an optimized plant, the energy and greenhouse gas emissions were nearly identical for coal and biomass, but a coal plant had much lower capital costs (Reichling and Klacki, 2011). Many different catalysts have been studied in Fisher Tropsch including (but not limited to) platinum (Davis et al., 2004), manganese (Chakrabarty et al., 1995), molybdenum (Adesina and Chen, 1994), and ruthenium (Dalai et al., 2008; Xiong et al., 2009), and zirconium (Ding and Wang, 2008). *Since liquid fuels are the target of Fisher Tropsch in this proposal, our efforts will focus on ruthenium, since it has been shown to make naptha-like molecules. However cobalt, a very common catalyst, will also be tested.*

Hydrotreating

Hydrotreating is used to upgrade bio-oils to high quality liquid fuels (Czernik and Bridgewater, 2004). Hydrotreating is necessary for most oils from biomass feedstocks because the oils contain too much oxygen to be useful fuels (Christensen et al., 2011). Hydrotreating is a catalytic process that often requires high temperatures (200-400 C) and high pressures (100-200 bar) in order to obtain reasonable production rates (Grange et al., 1996; Goudriaan and Peferoen, 1990). Many different types of reactors have been used in hydrotreating including slurry reactors (Zhang, 2003; Samolada et al., 1994), packed bed reactors (Elliot and Schiefelbein, 1989), and CSTR reactors (Elliot and Baker, 1984). In most of these applications, the temperature is near 350 C with pressures varying widely, from 15 – 300 bar, depending on the reactor type. It should be noted that deoxygenation efficiencies are typically 60-95%. Catalyst types affect the conversion, but the most commonly used are NiMo and CoMo. Elliott et al. (2009) found that using biomass feedstocks such as mixed wood, poplar, and corn stover heavy phase resulted in oil yields (g/g per dry feed) of 0.62, 0.59, and 0.78, respectively. *The Process Dynamics* *process, using Isotherming*^{TM}*, to dissolve hydrogen into a liquid, allows for the reactor to be operated much lower pressures with similar conversions, thus drastically reducing capital and operating costs. We will use temperature ranges (300-400 C) and catalyst types (CoMo and NiMo) that are commonly found in the literature and have been used successfully by Process Dynamics.*

Life Cycle Assessment

Despite the advantages of using heat integration in coal gasification and biomass pyrolysis it is still necessary to perform a detailed life cycle and technical economic assessment in the evaluation of a new processing scheme. Life cycle assessment has been performed in detail for both biomass pyrolysis and coal gasification. The most detailed study to date was by Carpentieri et al. (2011) who did a life cycle carbon balance review on many different biomass and coal conversion studies performed in literature. Their results showed that CO_2 removal was necessary for life cycle assessment. Without this CO_2 removal the specific emissions are actually worse than those from coal gasification. *However, none of these studies specifically dealt with heat integration, the focus of this proposed research, so we anticipate that the addition of heat integration will improve the emissions without an expensive* CO_2 *recovery process.*

Table 3: Specific Carbon Emission Comparison (biomass plants in bold) (Carpentieri et al.,

published results (table 6). **Reference**	**Specific CO_2 emission [kg/MWh]**	**Notes**
Present paper	**178**	**IBGCC + CO_2 removal (chemical absorption)**
Fiaschi and Lombardi 2001	725	Conventional ICGCC
Fiaschi and Lombardi 2001	130	ICGCC + CO_2 removal (chemical absorption)
Hendriks 1994	800	Conventional pulverised coal steam cycle (PCSC)
Hendriks 1994	760	Conventional ICGCC
Hendriks 1994	100	PCSC + CO_2 removal (chemical absorption)
Hendriks 1994	250	PCSC + CO_2 removal (membrane separation)
Hendriks 1994	40	ICGCC + CO_2 removal (chemical absorption)
Chiesa et al. 1999	709	Conventional ICGCC
Chiesa et al. 1999	73	ICGCC + CO_2 removal (chemical absorption)
Chiesa et al. 1999	71	ICGCC + CO_2 removal (physical absorption)
Chiesa and Consonni 1998	377	Conventional natural gas combined cycle
Chiesa and Consonni 1998	747	Conventional ICGCC
Chiesa and Consonni 1998	74	ICGCC + CO_2 removal (chemical absorption)
Lombardi 2003	388	Coal semi-closed gas turbine combined cycle (CSCGT/CC)
Lombardi 2003	65	CSCGT/CC + CO_2 removal (chemical absorption)
Mann and Spath 1997	**916**	**Conventional IBGCC**

TECHNICAL APPROACH

Overall Process

A block flow diagram of the proposed process for producing liquid transportation fuels from coal and biomass is shown in Figure 1. Coal will be ground and slurried (to about 50 wt%) with water and fed to the gasification reactor. The slurry feed rate will be adjusted to control the temperature of the gasifier between 1400-1500 C. The hot synthesis gas will be used to provide the heat required to heat the biomass to an optimum reaction temperature of about 550 C.

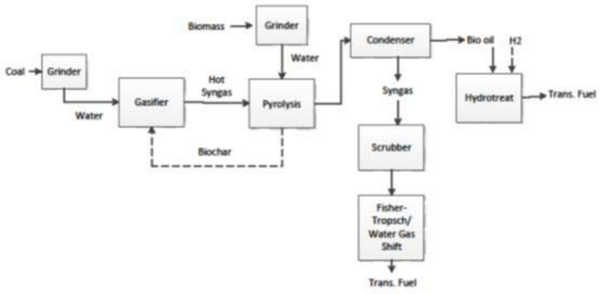


Figure 1: Arkansas Process for Conversion of Coal\Biomass to Liquid Fuels using Efficient Heat Integration

Biomass will be ground and slurried with water at about 35 wt%. The biomass slurry will be fed into the exit of the syngas reactor and mixed with the hot synthesis gas; its rate will control the mixture temperature about 550 C. The biomass pyrolysis reactor will be constructed of ½’ to 1” SS tube and it will be sized to give an optimum residence time with ½ to 1 second expected. The biomass pyrolysis reactor contains the produced bio-oils gases which are condensed, along with the contained water, in a direct contact condenser, using water as the heat sink. The pyrolysis oil will contain char and slag which will be removed by centrifugation. The centrifuged bio-oil are stored and processed in a later run to produce biobuel.

The synthesis gas from the direct contact condenser contains CO_2 and H_2S, which are removed by bubbling the gases through a NaOH solution. The cleaned syngas is sent to a two-stage Fischer-Tropsch reactor where the CO is first shifted to achieve a H_2:CO ratio of 2:1. The reactor 1st stage contains an iron catalyst which promotes the shift reaction of $H_2O + CO > H_2 + CO_2$; the 2nd stage reactor contains a cobalt catalyst which promotes the formation of hydrocarbons (primarily alkanes) and water from the CO and H_2.

The liquids from the Fisher Tropsch and the pyrolysis liquids are fed to an Isotherming® reactor where these liquids are reacted with hydrogen to saturate the molecules and remove the contained oxygen to produce liquid fuel.

Coal/Water Slurry Preparation

If available, ground coal will be purchased. If ground coal is not available conveniently, the coal will be ground and stored in 55 gallon drums or 1,000 lb tote bags. The ground coal will be slurried with water as needed in agitated 55 gallon drums. A 2 gpm piston or diaphragm pump with a discharge pressure capability of 750 psi will be used to feed the slurry to the gasification reactor.

Coal Synthesis Gas Reactor (CSGR)

Mechanical Details

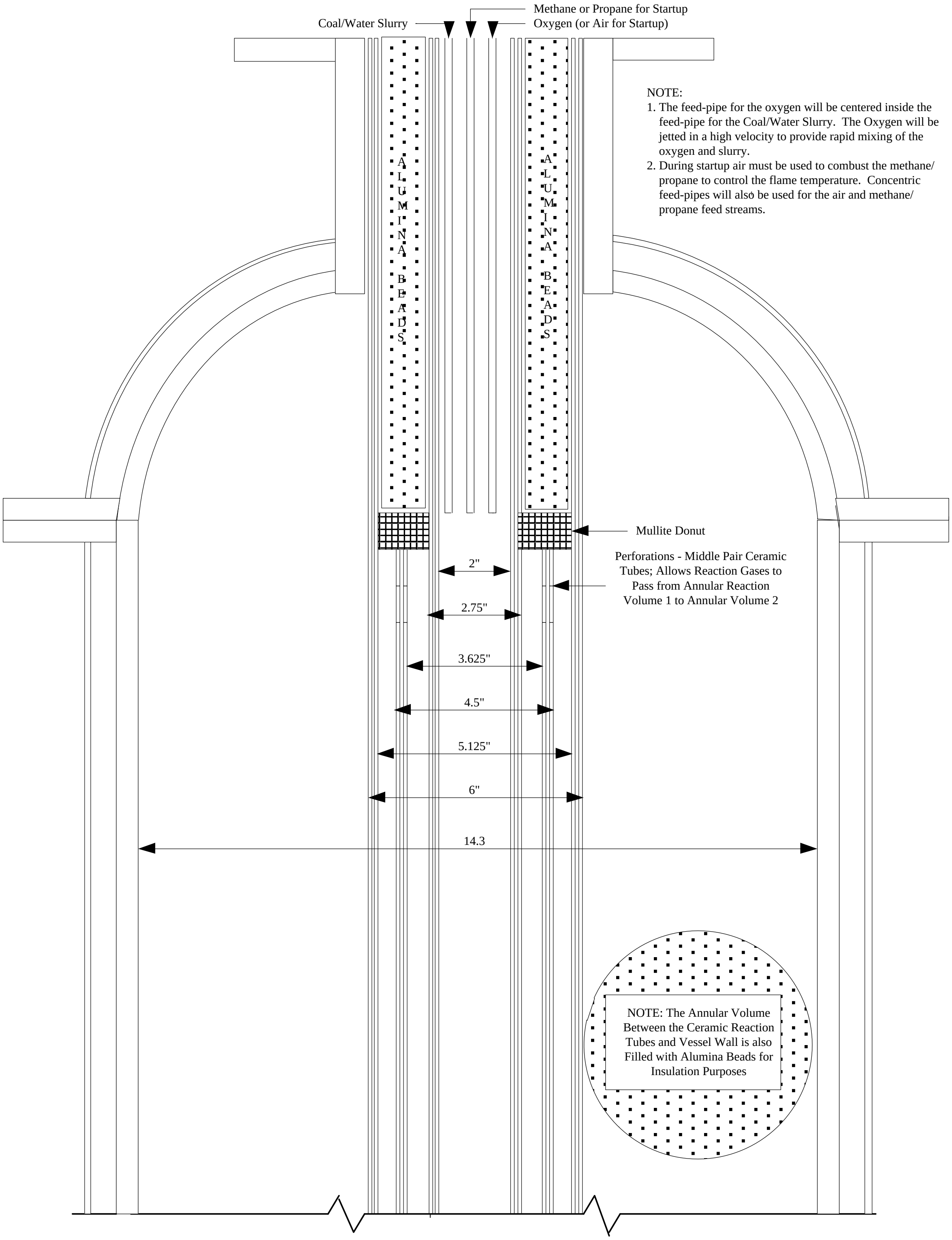
Figures 2a and 2b present mechanical drawings of the top and bottom of the CSGR. The CSGR is constructed within a 310 or 347 Stainless Steel, jacketed shell, which is fabricated from 16” Schedule 80 (14.31” ID; 16” OD; 0.84” wall thickness) pipe. At a design stress of 6,500 psi (at 700 C) the vessel will handle about 750 psig. The top and bottom heads are both flanged and jacketed. The overall height (i.e., length if the reactor is positioned horizontally) of the reactor will be about 10 m (33’).

Six nested ceramic (mullite [$3Al_2O_{3:}2SiO_2$]), from Coors Ceramics (http://css.coorstek.com) tubes varying in inside diameter from 2” to 5.625” ID are nested within the center of the reactor vessel to form three reaction chambers or zones. Each reaction zone is contained within the walls of ceramic tubes; The ID’s and OD’s of the 6 tubes are: 2”/2.25”; 2.375/2.75; 3.625/4; 4.125/4.5; 5.125/5.5; 5.625/6, respectively. Each bounding wall is constructed from two nested tubes because the tubes are only available in lengths up to 5’; thus, about 6 sections are required for one reactor pass and the joints need to be offset between the inner and outer tubes. The volume of the 1st reaction zone is 989 in^3 (0.57 ft^2, 0.016 m^3). The volumes of the 2nd and 3rd zones are 1.4 and 1.5 times the volume of the 1st chamber. The reactor volume between the outermost ceramic tube and the vessel walls will be filled with alumina beads to provide insulation between the ceramic reactor and the vessel walls.

At appropriate intervals (about 2 m [6.6’]) perforated mullite standoffs (in the form of donuts) will be provided to keep the nested tubes centered in the vessel shell. The reactor will also be operated using only the 1st reaction zone within the 2” ID center ceramic tube. The volume of the reactor in this configuration will be about 25% of the volume of the reactor when 3 reaction zones are utilized; thus, the reduced volume feed rates will be 25% of the full reactor volume feed rates.

The feed entry end of the CSGR (Figure 2a) has a centered nozzle on the head, which provides clearance for the outermost 6” OD ceramic tube to protrude to the top surface the nozzle. Three separate entry pipes are shown in Figure 2a. Only 2 feed pipes are planned. A concentric feed-pipe arrangement will be used for the oxygen and slurry; the oxygen will be introduced at high velocity though a center pipe and the slurry will be fed through a concentric pipe around the oxygen feed-pipe. A separate concentric pipe arrangement will be used for air and propane. The methane/propane will be fed through a center tube and the air will be fed through the concentric outer tube. The feed pipes must be cooled by encasing them with two annular zones with cooling provided by a molten salt solution flowing in (towards the feed-pipe tip) the outer annulus and out through the inner annulus. A typical nested feed pipe might consist of inner ¼” tubing inside a 3/8” tube, which is enclosed in a 5/8” tube inside a ¾” pipe.

In order to operate the reactor using all three reaction zones, the bottom of the center tube must be blocked (Figure 2b) and perforated (drilled holes) to cause the reaction gases to pass from down-flow in the 1 reaction zone to up-flow in the 2nd reaction zone. This blockage is accomplished by a mullite disk. As the reacting gases pass from the 2nd reaction zone to the 3rd reaction zone, they again must reverse direction from up-flow to down-blow; this is accomplished by a mullite donut located between the innermost ceramic tubes and the outer-most ceramic tubes. Alumina beads fill the cavity above the mullite donut up to the top of the ceramic tubes.



NOTE:
1. The feed-pipe for the oxygen will be centered inside the feed-pipe for the Coal/Water Slurry. The Oxygen will be jetted in a high velocity to provide rapid mixing of the oxygen and slurry.
2. During startup air must be used to combust the methane/propane to control the flame temperature. Concentric feed-pipes will also be used for the air and methane/propane feed streams.

NOTE: The Annular Volume Between the Ceramic Reaction Tubes and Vessel Wall is also Filled with Alumina Beads for Insulation Purposes

Figure 2a: Top of the Coal Synthesis Gas Reactor

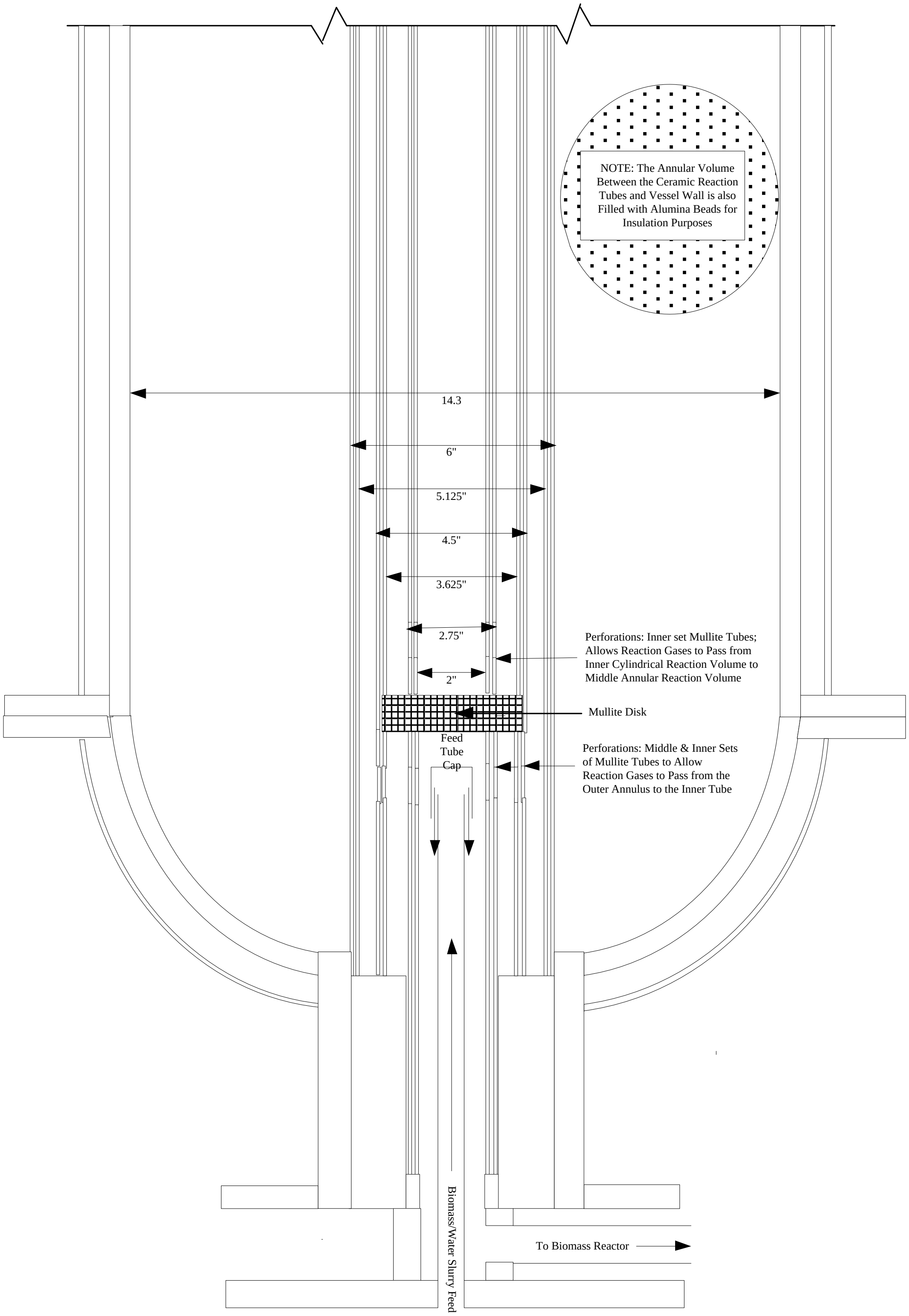
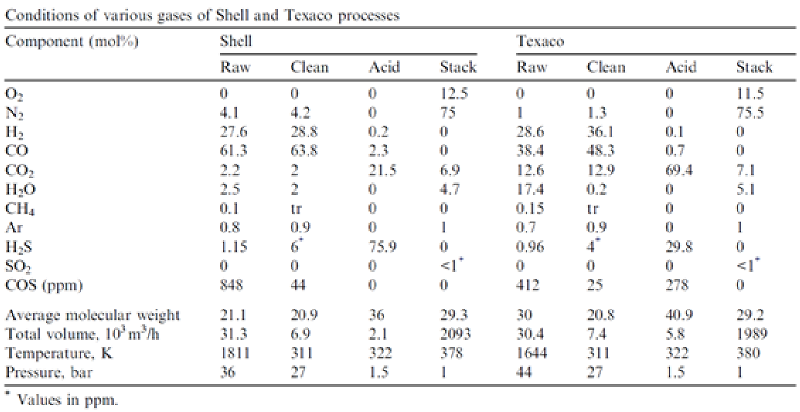


Figure 2b: Bottom of the Coal Synthesis Gas Reactor

At the bottom of the 3^{rd} reaction zone the hot reaction gases must exit the reactor. The exit occurs through perforations in the walls of the middle and inner ceramic tube(s). After passing through the two multi-walled ceramic tubes the gas stream must be mixed with the biomass/water slurry. This mixing is accomplished by injecting the biomass/water slurry through a centered feed-tube, which is capped at its top. The feed slurry will enter the reactor through the annulus between the feed tube cap and the outer feed-pipe wall. The feed will immediately mix with the hot synthesis gases, vaporize, cool to about 550 C and react in an external (to the CSGR) pipeline reactor.

The nozzle on the bottom head is shown in Figure 2b. It serves multiple purposes: it allows entry of the biomass/water slurry feed, supports and positions the six mullite tubes and allows the entire reaction mass to exit the reactor through an opening in its wall.

Table 4: Compositions of Raw Gases



Conditions of various gases of Shell and Texaco processes

Component (mol%)	Shell				Texaco			
	Raw	Clean	Acid	Stack	Raw	Clean	Acid	Stack
O_2	0	0	0	12.5	0	0	0	11.5
N_2	4.1	4.2	0	75	1	1.3	0	75.5
H_2	27.6	28.8	0.2	0	28.6	36.1	0.1	0
CO	61.3	63.8	2.3	0	38.4	48.3	0.7	0
CO_2	2.2	2	21.5	6.9	12.6	12.9	69.4	7.1
H_2O	2.5	2	0	4.7	17.4	0.2	0	5.1
CH_4	0.1	tr	0	0	0.15	tr	0	0
Ar	0.8	0.9	0	1	0.7	0.9	0	1
H_2S	1.15	6^*	75.9	0	0.96	4^*	29.8	0
SO_2	0	0	0	$<1^*$	0	0	0	$<1^*$
COS (ppm)	848	44	0	0	412	25	278	0
Average molecular weight	21.1	20.9	36	29.3	30	20.8	40.9	29.2
Total volume, $10^3 m^3/h$	31.3	6.9	2.1	2093	30.4	7.4	5.8	1989
Temperature, K	1811	311	322	378	1644	311	322	380
Pressure, bar	36	27	1.5	1	44	27	1.5	1

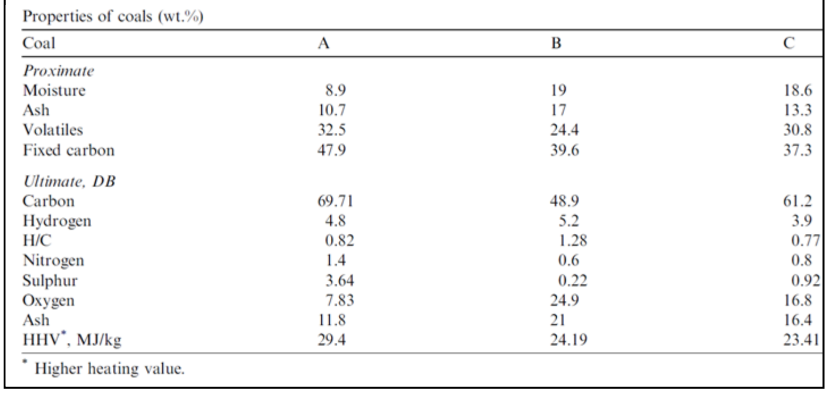
* Values in ppm.

The wall of the reactor must be maintained below about 700 C (1,300 F) to maintain a reasonable tensile strength; this is accomplished by circulating a molten salt solution (Vendor: http://www.bertrams-heatec.com) through the jacket. The jacket will have agitation nozzles with power dissipation of about 100 W/m^2 (about 5 kW for 50 m^2). Four agitation nozzles (spaced at about 2 m) will be used on the vessel straight side and one nozzle will be used on each of the vessel heads.

Process

The mass and energy balances for the syngas reactor are taken from Zheng and Furinsky. These authors have simulated the performance of a syngas reactor using the Aspen® Process Simulator for three coals (A – Prince Coal from Eastern Canada; B – Sub-bituminous from Alberta and C – Lignite from

Table 5: Properties of Coals



Properties of coals (wt.%)

Coal	A	B	C
Proximate			
Moisture	8.9	19	18.6
Ash	10.7	17	13.3
Volatiles	32.5	24.4	30.8
Fixed carbon	47.9	39.6	37.3
Ultimate, DB			
Carbon	69.71	48.9	61.2
Hydrogen	4.8	5.2	3.9
H/C	0.82	1.28	0.77
Nitrogen	1.4	0.6	0.8
Sulphur	3.64	0.22	0.92
Oxygen	7.83	24.9	16.8
Ash	11.8	21	16.4
HHV*, MJ/kg	29.4	24.19	23.41

* Higher heating value.

Saskatchewan). Coal A, which is close in composition to Illinois # 6 (Swanson, p. 8) is used here. The properties of Coal A are given in Table 5.

Reactor performance (at chemical equilibrium) is presented in Zheng and Furinsky as Table 4, which is included above. The composition of the raw gas from the Texaco process was used here.

There is sufficient information provided in Tables 4 and 5 from Zheng and Furinsky to determine the feed characteristics, except for the mass flow rates for this experimental apparatus. Table 6 provides those characteristics. The mass flows to the reactor must be determined based on the residence time required in the reactor. The residence time required at 1644 K (1371 C) is mentioned in the technical literature. Higman and Van Der Burgt (p. 130) state, *"The reactions are very fast, and after a residence time of 0.4 – 4 s the product gas leaves the reactor at the top, whereas, the slag leaves through an opening in the bottom of the reactor where is quenched in a water bath. The temperature in the gasifier is typically 1,500 C and the pressure is 30-40 bar."* And Shadle, L.J. et al. state, *"Entrained-flow gasifiers use high temperatures (1350 C – 1500 C) and gasify coals in 2-3 s."*

Table 6: Characteristics of the Feed for the Texaco simulation

Mass Ratio – Coal:Syngas	0.418
Mass Fraction Water in Slurry Feed	0.475
Volume Fraction Water in Slurry Feed+	0.541

\+ Based on a coal specific gravity of 1.3

A reasonable design criterion for the reactor residence time is 4 s. At full rate, with all three reaction zones used, the residence time in the 1st zone is about 1 s and in the last 2 zones about 3 s. Thus, for a 8 m long reactor the gas velocity (exit gas basis) in the 1st zone is 8 m/s. With a syngas density of 20 kg/m^3 and a cross-sectional area of the 2” ID tube of 0.002 m^2, the reactor will handle 584 kg/hr of syngas at 1644 K (1,371 C) and 44 atm (645 psia). Using this syngas production rate and the feed characteristics given in Table 6, the slurry feed to the reactor is fully defined in Table 7.

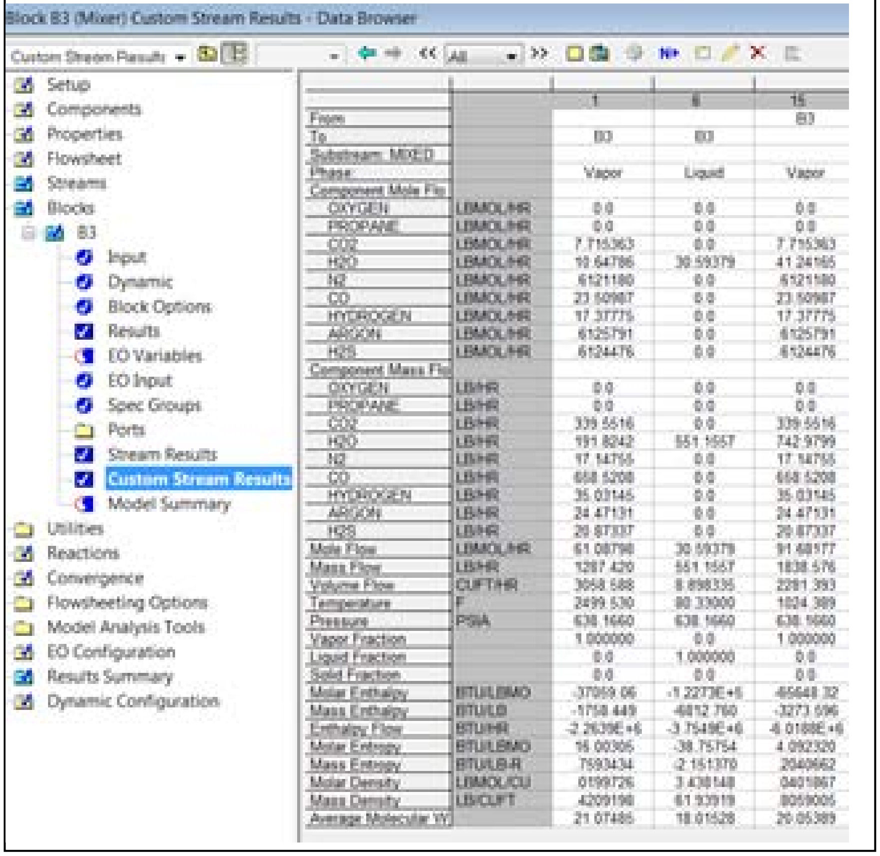
Table 7: Feed Slurry Parameters for the Syngas Reactor Operating at Full Rate Using all Three Reaction Zones.

Total Slurry Feed to Gasifier	465 kg/hr (1,023 lb/hr)
Coal Feed to Gasifier	244 kg/hr (537 lb/hr)
Water Feed to Gasifier	221 kg/hr (486 lb/hr)
Volumetric Slurry Feed to Reactor	1.8 gpm
Oxygen Feed to the Reactor	100 kg/hr (220 lb/hr)

Biomass Pyrolysis Reactor

After the synthesis gases leave the CSGR they must be mixed, cooled and reacted with the biomass in the water/biomass slurry. The synthesis gas must be cooled from 1371 C to 550 C as the biomass slurry is added. An ASPEN program was written to determine the water required to cool the reaction gases from 1371 C to 550 C. The results of that simulation are given in Table 8. The amount of water (less any biomass) required is 550 lb/hr (1.1 gpm). To the 550 lb/hr of water biomass can be added to bring the total of biomass slurry to about 846 lb/hr, giving a solids loading of 35%. Thus, 300 lb/hr of biomass can be processed, which gives a ratio of biomass to coal feed of 300/537 = 0.56. This is the maximum ratio which can reasonable be run; however, any ratio below this can also be accommodated.

Table 8: Results from an ASPEN Simulation of the Cooling of the Syngas Reactor Effluent from 1,371 C to 550 C (1,225 F)



		1	6	15
From				B3
To		B3	B3	
Substream: MIXED				
Phase:		Vapor	Liquid	Vapor
Component Mole Flo				
OXYGEN	LBMOL/HR	0.0	0.0	0.0
PROPANE	LBMOL/HR	0.0	0.0	0.0
CO2	LBMOL/HR	7.715363	0.0	7.715363
H2O	LBMOL/HR	10.64786	30.59379	41.24165
N2	LBMOL/HR	.6121180	0.0	.6121180
CO	LBMOL/HR	23.50987	0.0	23.50987
HYDROGEN	LBMOL/HR	17.37775	0.0	17.37775
ARGON	LBMOL/HR	.6125791	0.0	.6125791
H2S	LBMOL/HR	.6124476	0.0	.6124476
Component Mass Flo				
OXYGEN	LB/HR	0.0	0.0	0.0
PROPANE	LB/HR	0.0	0.0	0.0
CO2	LB/HR	339.5516	0.0	339.5516
H2O	LB/HR	191.8242	551.1557	742.9799
N2	LB/HR	17.14755	0.0	17.14755
CO	LB/HR	658.5208	0.0	658.5208
HYDROGEN	LB/HR	35.03145	0.0	35.03145
ARGON	LB/HR	24.47131	0.0	24.47131
H2S	LB/HR	20.87337	0.0	20.87337
Mole Flow	LBMOL/HR	61.08798	30.59379	91.68177
Mass Flow	LB/HR	1287.420	551.1557	1838.576
Volume Flow	CUFT/HR	3058.588	8.898335	2281.393
Temperature	F	2499.530	80.33000	1024.389
Pressure	PSIA	638.1660	638.1660	638.1660
Vapor Fraction		1.000000	0.0	1.000000
Liquid Fraction		0.0	1.000000	0.0
Solid Fraction		0.0	0.0	0.0
Molar Enthalpy	BTU/LBMO	-37059.06	-1.2273E+5	-65648.32
Mass Enthalpy	BTU/LB	-1758.449	-6812.760	-3273.596
Enthalpy Flow	BTU/HR	-2.2639E+6	-3.7549E+6	-6.0188E+6
Molar Entropy	BTU/LBMO	16.00305	-38.75754	4.092320
Mass Entropy	BTU/LB-R	.7593434	-2.151370	.2040662
Molar Density	LBMOL/CU	.0199726	3.438148	.0401867
Mass Density	LB/CUFT	.4209198	61.93919	.8059005
Average Molecular W		21.07485	18.01528	20.05389

The biomass reactor required residence time is less than one second; the velocity within the reactor should be adequate to transport the slag particles through the reactor. An estimated 75% of the synthesis gas from the biomass reactor will be flared; thus, only 25% of that gas will be fed to the biomass reactor. From the results of the ASPEN simulation (Table 8), about 570 ft^3/hr will enter the biomass reactor. At 50 ft/s the required reactor flow area is 0.5 in^2. Thus, a ½" Sch. 80 pipe, less than 50' long will suffice. Various length of biomass reactor will be tested to determine the maximum yield of bio-oils as residence time in the biomass reactor is varied.

When the syngas reactor is operated at lower feed rates when only the 1st zone reactor is used the ID of the biomass reactor should be decreased to about 25% of the diameter at the highest rates of syngas production. For this case, a reactor constructed of 3/8” or ½” OD tubing will be adequate.

The biomass reactor operates adiabatically; thus, it only requires the bare pipe and adequate insulation to satisfy the process requirements.

Direct Contact Condenser

Existing biomass reactors at Process Dynamics in Fayetteville and at Fig Tree Inc. in Sprindale use direct contact condensers to condense the bio-oils produced by the reactors. Each condenser consists of a cone-bottomed vessel, a circulating pump, a cooling coil within the vessel and a Spraying Systems spray nozzle in the reactor at its end. These successful units will be duplicated or enlarged as needed to satisfy the process requirements.

Centrifuge

An existing centrifuge will be used on a batch basis to separate the ash and slag from the produced bio-oils. The bio-oils will be stored for an entire pyrolysis run and they will be processed thorough the Isotherming® reactor subsequently.

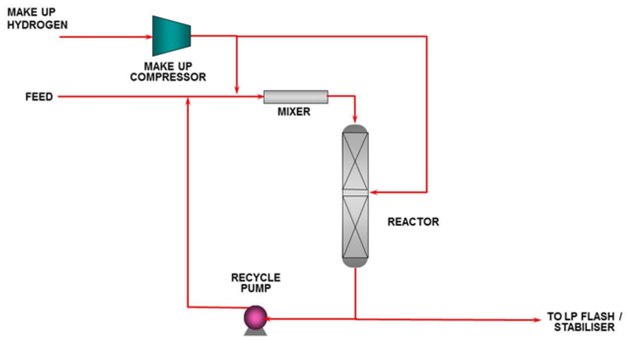


Figure 3: Isotherming® Technology

Hydrotreating The combined feeds of Fischer – Tropsch liquids and biomass pyrolysis liquids are to be hydrotreated using a process similar to the IsoTherming® hydroprocessing technology as shown in Figure 3. The IsoTherming® hydroprocessing technology is uniquely suited for hydrotreating feedstock containing large amounts of heteroatoms (oxygen in the case of pyrolysis oil). The process involves recycling hydrotreated liquid product. The recycle liquid acts as a carrier for hydrogen as well as a heat sink. If reactor conditions are such that 100 SCF of hydrogen is soluble in the feed to be hydrotreated, and, if the feed consumes 500 SCF of hydrogen, then four volumes of recycle would be necessary to carry the additional 400 SCF of hydrogen. This large amount of recycle would reduce the exotherm from the reactor by 80 percent.

Pyrolysis oils contain 30-40% oxygen by weight. This large amount of oxygen results in hydrogen consumptions of 3000 to 5000 SCR/bbl. Without cooling or quenching, the reactor exotherm would be on the order of 600 to 1000° F. Conventional hydrotreating technologies operate in a trickle bed fashion. The only cooling is by quenching with large amounts of cold hydrogen. Hydrogen, being so light, is not a very good heat sink. The large quantity of hydrogen recycle leads to large reactor diameters to keep the pressure drop down, and very large hydrogen recycle compressors both resulting in very high capital costs.

A schematic of the experimental hydrotreater is shown in Figure 4. The unit consists of three catalyst beds. Each is made of 2cm stainless steel tubing. The reactor tubes are each 30cm long and

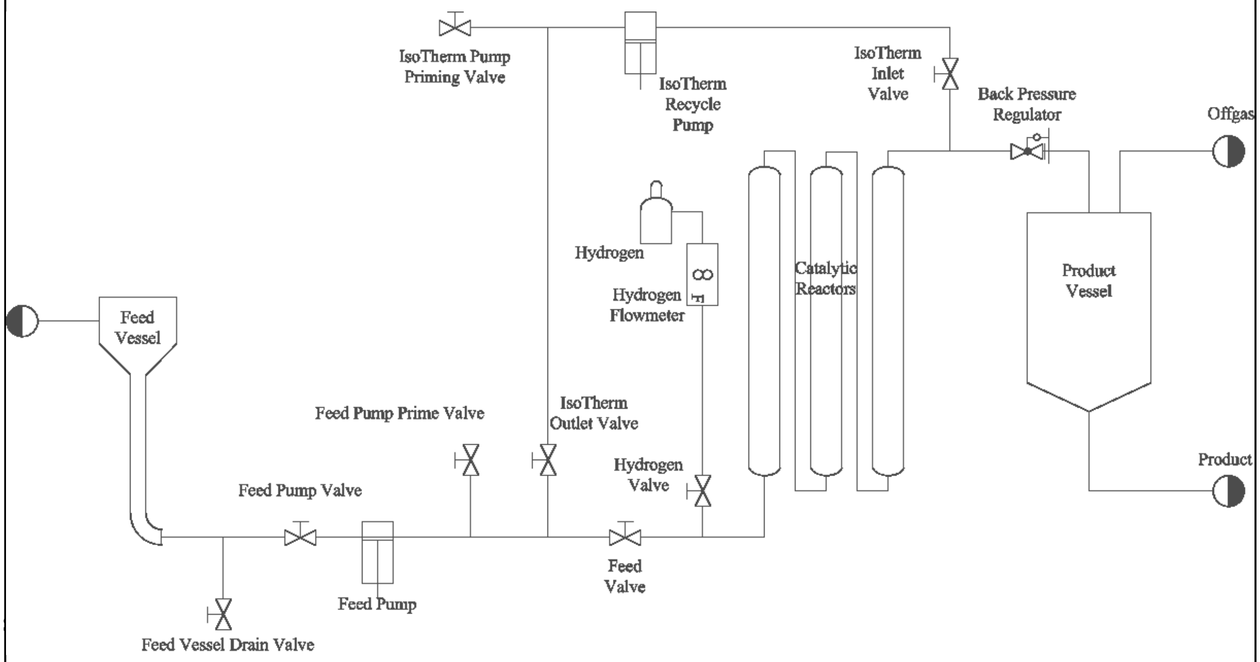


Figure 4: Hydrotreater System Schematic

the reactor tube and filled with sand. The baths are heated using electrical heat tape controlled by rheostats. Hydrogen is added to each bed through hydrogen mass flow controllers.

Liquid feed is fed to the unit using a piston metering pump. Liquid recycle is also accomplished using a piston metering pump. Fresh feed is fed to the unit and combined with hydrogen and liquid recycle. The combined feed then enters the first catalyst bed. Typical catalysts for hydrotreating are nickel moly (Nimo) on alumina or cobalt moly on alumina. The temperature in the bed is controlled by the hot sand bath. Typical hydrotreating temperature range is 450° F to 700° F. The pressure of the hydrotreaters will be the same as the gasifier temperature. Effluent from the first bed is combined with additional hydrogen and sent to a second catalyst bed where the additional hydrogen is consumed. Effluent form the second bed is combined with additional hydrogen and sent to a third bed. Effluent from the third bid is split with liquid recycle going back to the first bed and the net product going through a pressure control valve down to atmospheric pressure. The outlet from the control valve is sent to a separator. The vapors from the separator are measured and samples are taken for compositional analysis. Liquid samples are also taken for analysis.

An average run will consist of the following: The pyrolysis oil will be fed to the first bed at a rate of of approximately 7 ml/min. The pyrolysis oil will be mixed with recycled product which is being pumped at approximately 70 ml/min. The combined feed will be mixed with approximately 30 ml/min of hydrogen. The total blended feed of pyrolysis oil, recycle and hydrogen will be fed to the first catalyst bed containing a NiMo on alumina catalyst. The bed will operate at approximately 450 °F and a pressure equal to the gasification pressure. The outlet from the first bed will be mixed with an additional 30 ml/min of hydrogen and sent to a second bed of NiMo catalyst at a temperature equal to the first bed. The outlet from the second bed will again be mixed with 30 ml/min of hydrogen and sent to the third bed of NiMo catalyst at conditions equal to the first bed. The outlet of the third bed will be split into the liquid recycle stream and a net product stream which is flashed to one atmosphere. Liquid and vapor flow rates are measured and samples taken for analysis.

Fischer – Tropsch

The Fischer-Tropsch process involves the conversion of carbon monoxide (CO) and hydrogen (H_2) to alkanes; mostly via the following:

$$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ \underline{H_2O}$$

In addition to the formation of alkanes from CO and H_2; the water gas shift reaction is also important for increasing the ratio of H_2 to CO:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The optimum ratio of H_2/CO for producing alkanes is approximately 2. Typical synthesis gas obtained from the gasification of coal has a H_2/CO ratio of approximately 0.7. The water gas shift reaction can be used to adjust the H_2/CO ratio to about 2.0.

The Fisher-Tropsch system will be designed analogous to the Isotherming® Hydroprocessing System. Liquid hydrocarbon product will be recycled to the inlet of the fixed bed reactor and mixed with synthesis gas. The liquid recycle/synthesis gas are mixed in a static mixer so that all of the synthesis gas is dissolved in solution, no vapor enters the reactor. The large amount of liquid recycle, in addition to being a carrier of CO and H_2, acts as a large heat sink allowing the reactor to operate without a large temperature rise. The liquid recycle design is expected to give higher yields of liquid product in a single pass due to the large quantity of H_2 and CO dissolved at the reactor inlet and the lower temperature rise in the reactor. In addition, cooling of the recycle stream allows for the removal of water that is produced in the reactor.

The catalyst will be combination of iron, for water gas shift reactor, followed by a cobalt catalyst for Fisher-Tropsch reactor. The reactor will operate between 240-300 C and at pressures equal to the gasification reactor. The unit consists of three catalyst beds. Each is made of 2 cm stainless steel tubing. The reactor tubes are each 30 cm long and contained within a hot sand bath fabricated out of 5 cm diameter stainless steel pipe. The sand bath shell is constructed around the reactor tube and filled with sand. The baths are heated using electrical heat tape controlled by rheostats. Synthesis gas is added to each bed through mass flow controllers.

An average run will consist of the following: The synthesis gas will first be cleaned up using caustic. The gas will be bubbled through a column of caustic at ambient temperature and at a pressure equal to the gasification pressure. The clean synthesis gas will then be sent to the first catalyst bed at a rate of about 1000 ml/min. The first bed will be filled with an iron catalyst for the water gas shift reaction. The temperature of the first bed will be about 400 C. The gas from the first catalyst bed will be mixed with recycled liquid product from the third catalyst bed and sent to the second catalyst bed, containing a cobalt catalyst, at approximately 350 C. The liquid product from the second catalyst bed will be contacted with additional synthesis gas and sent to a third catalyst bed, also containing a cobalt catalyst at approximately 350 C. The products, both vapor and liquid, from the third catalyst bed will sampled and analyzed.

Facilities

A more complete description of the facilities, with pictures, is given in the Facilities section. Please refer to this section for pictures of piloting units and other details. Process Dynamics is located at 2435 Deane Solomon Road in Fayetteville, Arkansas, The companies facility consists of 6000 square feet of office space and 2500 square feet of laboratory and pilot plant space.

The lab facilities at Process Dynamics consists of three laboratories (wet lab, pilot plant, and analytical) totaling 2500 ft^2. The laboratory area is generally oriented toward small-scale testing of a variety of engineering processes and subsequent analysis of material products.

The pilot plant facility can implement process schemes by designing, constructing, and operating reactor vessels and associated equipment. Typically, pilot plant operating conditions require corrosive resistant materials capable of high temperature and high pressure applications. Process Dynamics routinely uses all stainless steel components in its pilot plants allowing operating conditions in excess of 700 F and 3000 psig. All the necessary tools are available on site to construct a pilot plant from basic materials. The pilot room is equipped with a fume hood, sink, and substantial 120 and 240 volt electric power. Cylinders supplying flammable, high pressure gas are located in a remote location allowing for safer operation of the pilot plant. Pilot plant operators continuously monitor operating conditions and this information is stored into digital format using data acquisition software.

The wet lab at Process Dynamics comprises multiple fume hoods and considerable bench top space. This area also contains gravity, forced air, and vacuum ovens. The wet lab is used for larger scale distillations, solvent extractions, liquid chromatography, and general laboratory work. A UV-VIS spectrometer, viscometers, penetrometer, and melt point apparatus is located here.

The analytical work area is primarily comprised of instrumentation but also contains a fume hood and sink. Two gas chromatographs are located here, each dedicated to a specialized analysis. These include simulated distillations of high and low boiling materials, composition determination of pilot plant off-gas, and speciation of sulfur and nitrogen components in a hydrocarbon matrix. Also located here is an x-ray fluorescence spectrometer used for the determination sulfur and metals in a variety of materials. This room also houses a refractometer for refractive index measurements and an analytical balance.

Statement of Project Objectives

A. Project Objectives

The overall goal of this proposal is to produce an environmentally friendly, flexible method for the use of coal for the production of biofuels and other valuable bio-intermediates and feedstocks. In contrast to much early reports, the work detailed in this proposal does not take the approach of using a coal/biomass feedstock, but instead uses a coal slurry/oxygen gasifier to generate hot synthesis gas which is in turn used to pyrolyze the biomass in a separate reactor. The low-grade liquid hydrocarbons from the pyrolysis reactor will be upgraded with a catalytic hydrogenation system. The design of the equipment is such that the first reactor can also be fed with a coal/biomass mixture. Specific technical goals of the proposed research include:

- *Test the concept of using waste heat from coal gasification for biomass pyrolysis*
- *Determine optimum coal\biomass ratios for maximum thermal efficiency*
- *Determine the possibility of recycling biochar from biomass pyrolysis into coal pyrolysis*

- *Use Fisher Tropsch to convert syngas into liquid fuel and hydrotreating to convert bio-oils into liquid fuels*
- *Show by life cycle assessment and energy balance that this process has a favorable energy and carbon balance.*

The goal of this project will be met by the performance of the following tasks:

1) A coal gasifier will be designed, constructed, and installed. This gasifier will be operated at various pressures, temperatures, coal/water compositions, coal/biomass/water compositions, fuel/oxygen ratios, fuel feed rates, residence time in the reactor, and biochar recycling. From the results of the various conditions, heat balances and product compositions will be determined.
2) A biomass pyrolysis reactor will be designed, constructed, and installed. This pyrolysis reactor will be fed biomass and biomass/coal mixtures at various rates and concentrations. Residence time of the feed in the reactor will also be studied.
3) The two reactors will be coupled and operated in tandem to experimentally determine the optimum conditions of synthesis gas generated in the first reactor to yield the most desirable product mix from the biomass pyrolysis reactor. The results of this task will be used to develop a process simulation useful for the extension of the system to differing biomasses. Additionally, a life cycle assessment will be performed on the overall process to ascertain the CO_2 emissions reduction of the newly developed system as contrasted to technology that is more prosaic.
4) A separation unit for condensing the liquids from the pyrolysis reactor and separating the hydrogen from the other gases will be designed, constructed and installed. A simple, water-cooled condenser will remove the liquids from the product stream. Some experimentation will be conducted to obtain good yields.
5) A reactor system will be designed, installed, and operated to accomplish the Fisher Tropsch catalytic conversion of the carbon monoxide and hydrogen to alkanes. A pre-treatment caustic spray tower will remove sulfides and carbon dioxide. A catalytic reactor will utilize the water shift reaction to increase the H_2/CO ratio. The catalyst for the water shift reaction will be iron.

Some experimentation will be conducted to determine the temperature, pressure, and residence time required to produce the desired H_2/CO ratio. The Fischer Tropsch system will be designed analogous to the Isotherming® Hydroprocessing System. Liquid hydrocarbon product will be recycled to the inlet of the fixed bed reactor and mixed with synthesis gas. The liquid recycle/synthesis gas are mixed in a static mixer so that all of the synthesis gas is dissolved in solution, no vapor enters the reactor. Cobalt will be used as the catalyst.

6) An Isotherming® catalytic hydrogenation reactor will be designed, constructed, installed, and operated for the purpose of up-grading low quality liquid hydrocarbons obtained from the tandem reactors and from the Fisher Tropsch reactor. The pyrolysis oil will contain char and slage which will be separated by centrifugation. The filtered bio-oil is then sent to hydrotreating where olefins are saturated and oxygen is removed, forming water, to form a product that can be fractionated into high quality transportation fuels. Variables to be studied will include the catalyst used, the temperature of the catalyst beds, the residence time of the feed in the catalyst beds, the recycle ratios, and the hydrogen feed rate. Data generated from operation of the Isotherming® reactor will be used to generate a kinetic model that will be useful in the design of commercial scale units.
7) A detailed economic analysis of the process will be conducted. Capital cost, operating costs, and scalability will be determined and compared to those for a coal-only process.
8) A LCA will be conducted to determine the overall “carbon footprint” of the proposed process. Results will be compared to those achieved with coal-only processes.

B. Project Scope

The proposed project will deliver a high yield system capable of producing vehicular fuels. This work will be different from earlier work in that the coal or coal/biomass gasifier will produce a hot synthesis gas that will be used in the biomass pyrolysis reactor. The production of the synthesis gas will be tailored so that the feed of biomass into the pyrolysis reactor will cool the synthesis gas to the optimum pyrolysis temperature. The carbon monoxide will be reacted with a part of the hydrogen in a Fisher Tropsch reactor, the rest of the hydrogen will be used in an Isotherming® hydrogenation reactor to upgrade liquids from the tandem reactors.

The proposed project has the potential to meet all of the requirements for Interest Area 1 of the RFP.

- The proposed system will be designed, built, installed, and operated so as to achieve a production rate of 2 liters per day or more.
- The proposed system will be used with a variety of low-level biomass feedstocks, and the coal/biomass ratios suitable for processing will be studied. Because of the tandem reactor arrangement of the proposed system, it is believed that the biomass/coal ratios achievable will be substantially higher than required in the RFP.
- The conversion chemistry will be indirect, with coal gasification to synthesis gas, followed by pyrolysis of the biomass, followed by Fisher Tropsch reaction, followed by Isotherming® hydrogenation
- The final product fuel liquids will be characterized by GC to determine the chemical profile of the liquids.
- The quality of the final product will be determined by ASTM standard methods.
- The commercial viability of the process will be studied with a detailed economic analysis of the process, using good engineering practices, and comparing the analysis with processes not employing the biomass and Isotherming® hydrogenation aspects.
- An LCA of the process will be conducted to determine the “carbon footprint” of this proposed process relative the coal-only processes.
- A minimum of one one-liter sample will be provided to the funding agency

C. Tasks to be Performed

1. ***Project Management Plan -*** This task includes all work elements required to maintain and revise the Project Management Plan, and to manage and report on activities in accordance with the plan.

2. ***Kick-off Meeting* –** This includes the kick-off meeting and yearly meetings with the DOE. Ackerson will lead this effort and Hestekin will be secondary. ***Coal Gasifier (months 0-35)* -** This unit will be completely operational at the conclusion of the first year of funding. Its purpose is to produce the coal slurry, generate synthesis gas of a composition suitable for use in the biomass pyrolyzer, and to provide heat sufficient to operate the biomass pyrolysis unit.
3. Design (months 0-2)
    - 3.1.1. The preliminary conceptual design of the syngas reactor has already been done in support of this proposal. The concept drawings provided with this proposal will be used to provide the information needed to design the reactor to meet ASME code requirements. The coal grinding and slurry portion of the process involves well-known unit operations. Good engineering practices, especially those related to safety and environmental hazards will be employed.
    - 3.1.2. The coal gasifier to be constructed is massively over-designed with respect to capacity. This is due to the very difficult technical problems involved in the design of very small reactors and their ancillary equipment. The current design is felt to be the smallest unit that can be constructed that will operate reliably without danger of system plugs or the requirement of very tiny, specialized slurry pumps, very small diameter feed & transfer lines, and other equipment. It is estimated that the coal gasifier designed for the proposed work will handle a maximum coal feed rate of about 500 pounds/hour..
    - 3.2. *Procurement/Construction (months 1-7)* **-** The unit will be constructed in an ASME certified shop, as skid mounting would increase the cost. The construction of the unit will be done to facilitate maintenance and modification.
    - *3.3. Operation (months 8-34)*
        - 3.3.1. In practice, a small amount of the synthesis gas from the coal gasifier will be used by the biomass pyrolyzer. The remainder of the synthesis gas will be flared.

3.3.2. The operation of the coal gasifier will be continuous.

3.3.3. An Aspen Plus simulation will be developed to model the outflow chemical composition and the heat and mass balances of the gasifier.

3.3.4. The unit will be operated as a stand-alone unit only long enough to determine the validity of the simulation of subtask 1.3.3. Subsequent operation will be in tandem with the operation of the biomass pyrolyzer.

3.4. *Analysis (months 30-35)* - The results of the coal gasifier operation within the integrated system will be subjected to critical analysis. Trends in synthesis gas composition and heat transfer from the unit to the biomass pyrolyzer as functions of input flow rates, pressure, temperature, and outlet flowrates will be determined. From this trend analysis, operating conditions for the coal gasifier to best support the requirements of the biomass reactor will be determined. These conditions will then be used in tasks 7, economic analysis and 8, LCA.

3.5. *Responsible Investigator* - Ackerson will lead this effort with secondary leads Clausen and Penney. A Process Dynamics Engineer will support the task.

3.6. Go-NoGo – At the end of month 12, this unit will be operational and producing synthesis gas. ***This is a go\no-go decision point.***

4. Biomass Pyrolysis

4.1. Design (months 0-2)

4.1.1. Much of the design effort has already been reported in the literature. These designs will be reviewed and form the basis of our proposed unit. Concept drawings will be generated and reviewed, and then will be used to finalize construction drawings, prepare material lists, and provide opportunity for a pre-construction technical review. Good engineering practices, especially those related to safety and environmental hazards will be employed.

4.1.2. The biomass pyrolysis unit will be sized to generate the required 2 liters per day of final product fuel.

    - 4.1.3. The design will incorporate hardware and operational protocols to facilitate the analysis of the products flowing from the reactor.
- 4.2. *Procurement/Construction (months 1-6)* - The unit will be constructed in place. The construction of the unit will be done to facilitate maintenance and modification.
- *4.3. Operation (months 7-34)*
    - 4.3.1. The operation of the biomass pyrolysis reactor will be continuous.
    - 4.3.2. An Aspen Plus simulation will be developed to model the input streams, the outflow chemical composition and the heat and mass balances of the pyrolyzer.
    - 4.3.3. The initial trial runs of the biomass pyrolysis unit will be done with surrogate feedstocks.
    - 4.3.4. The unit will be operated as a stand-alone unit only long enough to determine the validity of the simulation of subtask 2.3.2. Subsequent operation will be in tandem with the operation of the coal gasifier.
- 4.4. *Analysis (months 30-35)* - The results of the biomass pyrolysis operation within the integrated system will be subjected to critical analysis. Trends in pyrolysis product composition as functions of input flow rates and composition, pressure, temperature, and outlet flowrates will be determined. From this trend analysis, operating conditions for the pyrolyzer to best support the requirements of the Fisher Tropsch and Isotherming® reactors will be determined. These conditions will then be used in tasks 7, economic analysis and 8, LCA.
- 4.5. *Responsible Investigator* - Hestekin will lead this area while Penney and Ackerson will be secondary. A PhD student will perform the work.
- 4.6. Go-NoGo – At the end of month 12, this unit will be operational and producing synthesis gas. ***This is a go\no-go decision point.***

5. *Reactor Interfacing*

- *5.1. Design (months 2-3)*

5.1.1. This design will ensure that the coal gasifier products are properly split so that one stream will support the operation of the biomass pyrolyzer and the rest of the gas will be safely flared.

5.1.2. The design will ensure that temperatures and pressures delivered from the coal gasifier will be delivered to the biomass pyrolyzer with little or no degradation.

5.1.3. The design will incorporate hardware and operational protocols to facilitate the analysis of the products flowing to the biomass pyrolysis reactor.

5.2. *Procurement/Construction (months 6-7)* - The unit will be constructed in place. The construction of the unit will be done to facilitate maintenance and modification.

5.3. *Operation (months 8-34)* - This subsystem will be used throughout the project whenever the coal gasifier and biomass pyrolysis reactors are operated in tandem.

5.4. *Analysis (months 30-35)* - No critical analysis is planned for this subsystem.

5.5. *Responsible Investigator* - Responsible Investigator – Penney will lead this area, Ackerson will be secondary. A Process Dynamics Engineer will perform the work.

5.6. Go-NoGo – There is no Go/NoGo decision point for this task.

6. *Product Separation*

6.1. *Design (months 2-3)*

6.1.1. Much of the design effort has already been reported in the literature. These designs will be reviewed and form the basis of our proposed unit. Concept drawings will be generated and reviewed, and then will be used to finalize construction drawings, prepare material lists, and provide opportunity for a pre-construction technical review. Good engineering practices, especially those related to safety and environmental hazards will be employed.

6.1.2. This unit will incorporate a centrifuge to separate biochar for recycling to the coal gasifier.

6.2. *Procurement/Construction (months 7-8)* - The unit may be constructed in place, or if suitable off-the-shelf hardware is available, the unit or its pieces may be purchased and the pieces assembled on-site. The construction of the unit will be done to facilitate maintenance and modification.

6.3. *Operation (months 9-34)* - This unit will be operated whenever the biomass pyrolyzer is operational.

6.4. *Analysis (months 30-35)* - Minimal trend analysis will be required for this subsystem. In the unlikely event that the system proves inadequate for recovery of the pyrolysis products, it will be modified as needed.

6.5. *Responsible Investigator* - Hestekin will lead this task, Ackerson and Clausen will be secondary. A PhD student will perform the work.

7. *Fisher Tropsch*

7.1. Design (months 0-1)

7.1.1. The design of Fisher Tropsch has been reported extensively in the literature. These designs will be reviewed and form the basis of our proposed unit. The design of our system will be very similar to that of the Isotherming® reactor discussed in task 6. Concept drawings will be generated and reviewed, and then will be used to finalize construction drawings, prepare material lists, and provide opportunity for a pre-construction technical review. Good engineering practices, especially those related to safety and environmental hazards will be employed.

7.1.2. The design will include a pretreatment system, spraying the incoming products stream with caustic solution to remove sulfide gases and carbon dioxides, which are catalyst poisons.

7.2. *Procurement/Construction (months 2-3)* - The hardware and tools necessary for the construction of this module are in place, so the reactor will be constructed in place, and will require very little time. The construction of the unit will be done to facilitate maintenance and modification.

7.3. *Operation (months 5-34)* - This unit will typically be operated in tandem with the biomass pyrolysis unit.

7.4. *Analysis (months 30-35)* - The results of the Fisher Tropsch operation will be subjected to critical analysis. Trends in product composition as functions of input flow rates and composition, pressure, temperature, and outlet flowrates will be determined. From this trend analysis, operating conditions for the the Fisher Tropsch reactor will be determined. These conditions will then be used in tasks 7, economic analysis and 8, LCA.

7.5. *Responsible Investigator* - Clausen will lead this area while Ackerson and Penney will be secondary. A post-doctoral fellow will perform the work.

7.6. Go-NoGo – At the end of month 12, this unit will be operational and producing synthesis gas. ***This is a go\no-go decision point.***

8. *Isotherming® Hydrogenation*

8.1. *Design (done)* - No design work is necessary, as the designs, hardware, and tools are already in-place.

8.2. *Procurement/Construction (months 2-3)* - The hardware and tools necessary for the construction of this module are in place, so the reactor will be constructed in place, and will require very little time. The construction of the unit will be done to facilitate maintenance and modification, and for the use of different catalysts.

8.3. *Operation (months 10-34)* -This unit will typically be operated in tandem with the biomass pyrolysis unit.

8.4. *Analysis (months 30-35)* - The results of the Isotherming® operation will be subjected to critical analysis. Trends in product composition as functions of input flow rates and composition, pressure, temperature, outlet flowrates, and catalyst identity will be determined. From this trend analysis, operating conditions for the Isotherming® reactor will be determined. These conditions will then be used in tasks 7, economic analysis and 8, LCA.

8.5. Responsible Investigator - Ackerson will lead this area, Penney will be secondary. A post-doctoral fellow will perform the work.

8.6. Go-NoGo – At the end of month 12, this unit will be operational and producing synthesis gas. ***This is a go\no-go decision point.***

9. ***Economic Analysis (months 30-35)***

    9.1. *Capital Costs* - The capital costs of a 10,000 barrels per day (BPD) system will be determined using good engineering practices as detailed by Peters, Timmerhaus, and West. The analysis of results from tasks 1, 2, 4, 5, and 6 will be used.

    9.2. *Operating Costs* -The operating costs of a 10,000 barrels per day (BPD) system will be determined using good engineering practices as detailed by Peters, Timmerhaus, and West. The analysis of results from tasks 1, 2, 4, 5, and 6 will be used.

    9.3. *Return on Investment* - Return on investment will be determined for the 10,000 BPD plant will be determined using good engineering practices as detailed by Peters, Timmerhaus, and West. The results of subtasks 7.1 and 7.2 will be used.

    9.4. *Comparison to Coal-Only Processes* - The results of subtasks 7.1, 7.2, and 7.3 will be compared and contrasted with similar numbers from coal-only systems to be found in the literature.

    9.5. *Responsible Investigato*r - Clausen will lead this area and Hestekin will be secondary. A PhD student will perform the work.

10. ***Life Cycle Assessment (months 30-35)*** **-** A life cycle assessment will be performed using SIMAPRO after the ASPEN simulation. Jamie Hestekin at the University of Arkansas has experience with this software and will perform the life cycle assessment, and will be responsible for this task.

D: Deliverables

One one-liter sample of prepared fuel will be provided. Other samples may be delivered upon mutual agreement between the Principle Investigator and the contracting agency. Reports and other deliverables will be provided in accordance with the Federal Assistance Reporting Checklist following instructions therein. Other deliverables from the project include:

- ASPEN simulation of a working system to use coal and biomass to make liquid fuels.

- Design plans of a working system to use coal and biomass to make liquid fuels.
- A complete energy balance of a working system to use coal and biomass to make liquid fuels.
- A complete scaled up cost analysis of a working system to use coal and biomass to make liquid fuels.
- A complete life cycle assessment of a working system to use coal and biomass to make liquid fuels.
- Recommendations for how to improve the system for use of coal and biomass into liquid biofuels.