AN INTEGRATED APPROACH TO HYDROGEN PRODUCTION FROM AGRICULTURAL RESIDUES FOR USE IN URBAN TRANSPORTATION

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Abstract

This project focuses on the use of agricultural residues such as peanut shells to produce hydrogen for urban transportation. Specifically, a side stream of the pyrolysis products of a process for making activated carbon from densified peanut shells at Scientific Carbons Inc. in Southwest Georgia will be used to test the concept. The primary focus of this work was to undertake process development studies in the use of the large quantities of peanut shells produced in Georgia as feedstock for the pyrolysis-steam reforming process. The method combines two stages: slow pyrolysis of biomass to generate charcoal and catalytic steam reforming of the pyrolysis vapors to hydrogen and carbon dioxide. Scientific Carbons Inc. is currently operating a pilot facility in Blakely, GA to convert 24 tons/day of pelletized peanut shells to activated carbon. Scientific Carbons' facility will be used to perform a scaled-up demonstration of a steam reforming process to convert the off-gas of the peanut shell carbonization process to hydrogen. As a small company with the demonstrated ability to build modular systems, their current processes could be modified and expanded to run a variety of other feedstocks and to make a range of alternative products. This year we focused on development of decision models for selecting feedstock, process and alternatives, and the design and management of the construction of a 7-kg/hr fluidized-bed catalytic reactor system. The catalytic reactor system was successfully constructed and shipped to NREL. Shakedown runs of the system are expected to be completed in summer 2001.

Introduction

Background

Hydrogen is the most environmentally friendly fuel and can be efficiently used for stationary power and mobile applications. When burned or oxidized, it generates water as the only emission (small amounts of NOx are generated during the combustion process but can be controlled to very low levels). At present, hydrogen is produced almost entirely from fossil fuels such as natural gas, naphtha, and coal. During these hydrogen production processes, large amounts of fossil-derived CO_2 are released to the atmosphere. Renewable biomass is an attractive alternative to fossil feedstocks because of essentially zero net CO_2 impact [1].

Biomass is defined as a material that has participated in the "growing cycle." Agriculture waste, forest residue, urban wood waste, and trees and grasses grown as energy crops are materials commonly referred to as biomass. Because biomass consumes as much CO_2 in the growing cycle as is produced when it is transformed into energy, the net CO_2 contribution from biomass-derived fuels is considerably less than from fossil-derived fuels. In addition, producing biomass on a sustainable basis by growing energy crops will support Georgia's agricultural sector, an important part of the state's economy. Successful commercialization of this technology will also reduce oil and gas imports of the U.S. [1].

Agriculture is Georgia's largest industry and contributes over $46 billion to the state's annual economic output. One in six Georgians work in an agriculture-related sector. Georgia ranks as the number one state in the U.S. in peanut production, producing about 45% of all peanuts grown in the U.S. Georgia farmers grew about 1.5 billion pounds of peanut in 79 counties in 1999. Disposal of the large quantity of peanut shells in an environmentally acceptable manner is a significant challenge for the peanut industry. Hence peanut shells have been targeted as a feedstock for conversion to hydrogen.

The National Renewable Energy Laboratory (NREL) in Golden, CO has developed the basis of a technology for the generation of hydrogen from biomass and agricultural residue [2,3]. Biomass can be converted to hydrogen by two distinct strategies: 1) gasification followed by shift conversion and 2) pyrolysis of biomass to form a bio-oil that can be subsequently converted to hydrogen via catalytic steam reforming and shift conversion. The NREL technology uses the latter approach, which has the potential to be cost competitive with current commercial processes for hydrogen production [4]. The process has been demonstrated at the bench scale using model compounds and the carbohydrate-derived fraction of bio-oil [2,3]. This concept has several advantages over the traditional gasification technology. Bio-oil is easily transportable so the second step (steam reforming) can be carried out at a different location, close to the existing infrastructure for hydrogen use or distribution. The second advantage is the potential for production and recovery of higher-value co-products from bio-oil that could significantly impact the economics of the entire process.

The bio-oil produced from fast pyrolysis of biomass contains about 75-85 wt% organics and 15-25% water [2,3]. The latter is the result of the moisture content in the biomass feed and dehydration reactions which proceed in parallel with the thermal depolymerization reaction. The

organics are generally a mixture of aldehydes, alcohols and acids derived from the carbohydrate fraction of biomass, and phenolics derived from the lignin fraction. Fast pyrolysis produces a bio-oil made up of two distinct fractions: a monomer-rich aqueous fraction (containing typically 20 wt% organics) and a hydrophobic fraction composed mainly of oligomers derived from lignin. Steam reforming can be used to convert the entire bio-oil or each of the fractions of the oil.

The hydrogen content in biomass is relatively low (6-6.5%), compared to almost 25% in natural gas. For this reason, producing hydrogen via the biomass gasification/water-gas shift process cannot compete on a cost basis with the well-developed commercial technology for steam reforming of natural gas. However, an integrated process, in which part of the biomass is used to produce more valuable materials or chemicals and the residual fractions are used to generate hydrogen, can be an economically viable option.

The overall steam reforming reaction of bio-oil or any oxygenated organic compound with a chemical formula of $C_nH_mO_k$ can be represented as:

$$C_nH_mO_k + (2n-k)H_2O = nCO_2 + (2n+m/2-k)H_2$$
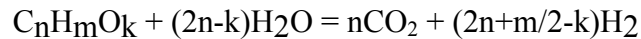
The stoichiometric yield of hydrogen is $2+m/2n-k/n$ moles per mole of carbon in feed. A mass balance of the NREL approach using fast pyrolysis is shown in Figure 1.
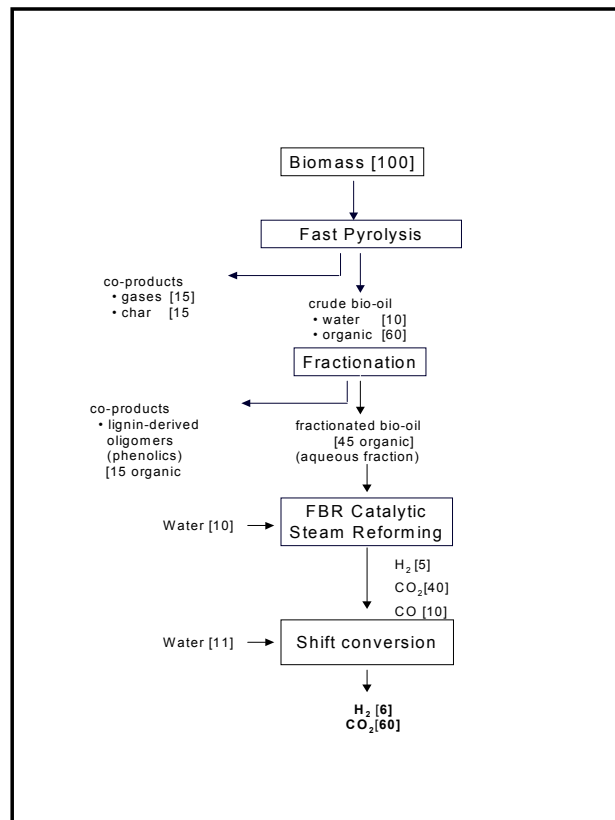

Figure 1. NREL Biomass to Hydrogen Process based on fast pyrolysis with phenolic coproducts.

Prior Work

In previous years it was demonstrated, initially through micro-scale tests then in the bench-scale fixed-bed reactor experiments [2,5,6], that bio-oil model compounds as well as the carbohydrate-derived fraction of bio-oil can be efficiently converted to hydrogen. Using commercial nickel catalysts the hydrogen yields obtained approached or exceeded 90% of those possible for stoichiometric conversion. The carbohydrate-derived bio-oil fraction contains a substantial amount of non-volatile compounds (sugars, oligomers) which tend to decompose thermally and carbonize before contacting the steam reforming catalyst. Prior studies managed to reduce these undesired reactions by injecting the oil fraction to the reactor in a form of a fine mist. However, the carbonaceous deposits on the catalyst and in the reactor freeboard made most of the catalyst inaccessible to contact with the oil, limiting the reforming time to 3-4 hours. For the above reasons, NREL decided to employ a different reactor configuration, a fluidized bed, to overcome at least some limitations of the fixed-bed unit. This greatly increased the reforming efficiency and extended the catalyst time-on-stream. Catalyst regeneration was done by steam or carbon dioxide gasification of carbonaceous residues providing additional amounts of hydrogen.

Experiments at NREL

Pelletized peanut shells were obtained from Scientific Carbons Inc. in Georgia. These materials were pyrolyzed at the NREL Thermochemical Users Facility (TCUF) using the fast ablative pyrolysis system (vortex reactor). The reactor wall temperature was maintained within the range of 600-625°C, which has been proven to provide the highest bio-oil yield. Nitrogen at a flow rate of 15 kg/h was used as the carrier gas for the biomass particles in the pyrolysis reactor. The tests proceeded smoothly at the rate of 10 kg/h. Eventually, 200-300 kg of pyrolysis oil was generated from feedstock. Peanut shell oil was collected in the scrubber of the pyrolysis system as a two-phase liquid (water was used for scrubbing pyrolysis vapors), with the top fraction containing 32.3% organics (6% are lignin-derived oligomers) and 67.7% water. Water content of the liquids was determined by Karl-Fisher titration method using a Metrohm 701 KF Titrino analyzer. Elemental composition, including the carbon, hydrogen, and oxygen content of these liquids was analyzed by a commercial laboratory (Huffman Laboratories, Golden, CO). The aqueous solutions were then used in reforming tests to produce hydrogen.

Fluidized Bed Reforming System

The experiments were carried out using a bench-scale fluidized-bed steam reformer. The schematic of the fluidized bed system is shown in Figure 2. The two-inch-diameter Inconel reactor supplied with a porous metal distribution plate was placed inside a three-zone electric furnace. The reactor contained 150-200g of commercial nickel-based catalyst from UCI (C11-NK) ground to the particle size of 300-500μm. The catalyst was fluidized using superheated steam, which was also a reactant in the reforming process. Steam was generated in a boiler and superheated to 750°C before entering the reactor at a flow rate of 2-4 g/min. Liquids were fed at a rate of 2-5 g/min using a diaphragm pump. A specially designed oil injection nozzle supplied with a cooling jacket was used to spray liquids into the catalyst bed. The oil temperature in the injector was controlled by a coolant flow and maintained below boiling point to prevent premature evaporation of volatiles and consequent deposition of nonvolatiles. The condensate was collected in a vessel whose weight was continuously monitored. The outlet gas flow rate

was measured by a mass flow meter and by a dry test meter. The gas composition was analyzed every 5 minutes by an MTI gas chromatograph. The analysis provided concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and nitrogen in the outlet gas stream as a function of time. The temperatures in the system as well as the flows were recorded and controlled by the OPTO data acquisition and control system.
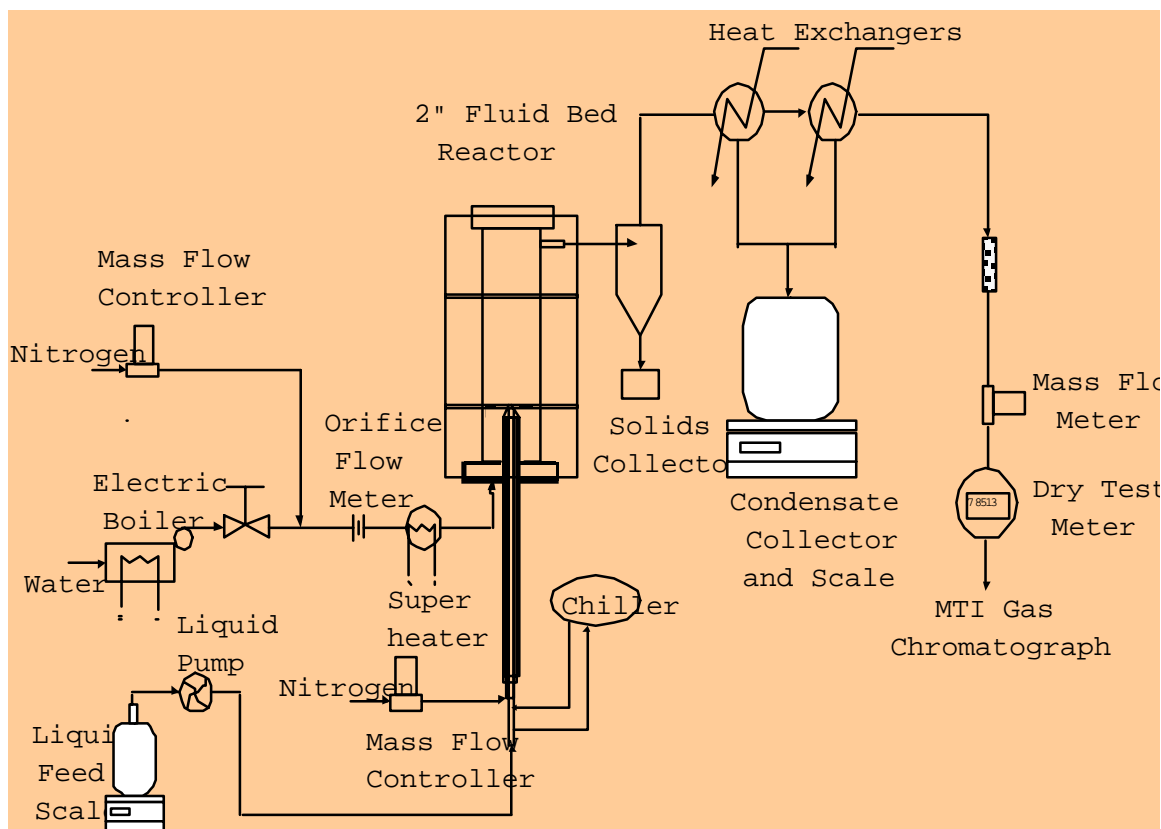

Figure 2. Schematic of the fluidized bed reforming system.

The measurements allowed determination of the total and elemental balances for the reforming tests as well as the calculation of the yield of hydrogen generated from the biomass-derived liquid feed. The maximum (stoichiometric) yield of hydrogen was $2+m/2n-k/n$ moles per mole of carbon in feed. Therefore, 63 g of hydrogen could be theoretically obtained from 1 L of peanut shell oil extract. The steam reforming experiments in the fluidized bed reactor were carried out at the temperature of 800°C and 850°C. The steam to carbon ratio varied from 7 to 13, while the methane-equivalent gas hourly space velocity $G_{C1}HSV$ was in the range of 1200-1500 h^{-1}. Gas composition (on nitrogen free basis) obtained from the peanut shell pyrolysis oil is shown in Figure 3. During eight hours of the experiment, the gas composition was very stable and only a small decrease in the concentration of hydrogen and an increase in methane were observed.

Methane concentration, though it grew to 3000-4000 ppm, still remained an order of magnitude smaller than that of the three major gas components and, therefore, is not shown in Figure 3. More fluctuation was observed in the amount of gas produced and, consequently, in the yield of hydrogen from the peanut bio-oil fraction, which is presented in Figure 4. The hydrogen yield

was still at the level of 80% of the stoichiometric potential after eight hours on stream. Peanut shell liquid had a higher concentration of the organic compounds, especially of lignin oligomers than the wood oil fractions. Large molecules of lignin compounds are less reactive and probably required a longer contact time with the catalyst than the smaller carbohydrate-derived fragments. They are also more likely to form carbon deposits on the catalyst surface. However, at 850°C, these deposits were removed and converted to hydrogen and carbon oxides by steam processing with the same efficiency as that observed for wood-derived liquids (carbon to gas conversion of 92%). This resulted in hydrogen yields greater than 80% of the stoichiometric potential during eight-hour catalyst time on stream.

The yields of hydrogen would be 5-7% higher if the reforming was followed by water-gas shift processing of carbon monoxide in the product gas. The global mass balance closure for the whole experiment was 94%, and 88-91% of bio-oil carbon was converted to gases. Both the decrease in the hydrogen production and the missing carbon in the mass balance suggest that a small part of the carbon from bio-oil formed deposits on the catalyst surface. Steam treatment of the used catalyst performed at 850°C resulted in the release of hydrogen and CO_2 in the amount corresponding to 4-5% of the carbon fed (about half of the missing carbon). The other part of carbon unaccounted for was probably entrained by product gases together with the catalyst fines and collected in the cyclone and condensers. The steam treatment - by removing deposits from the surface - also regenerated the catalyst, which performed during the following test at the same level of activity as the fresh catalyst.
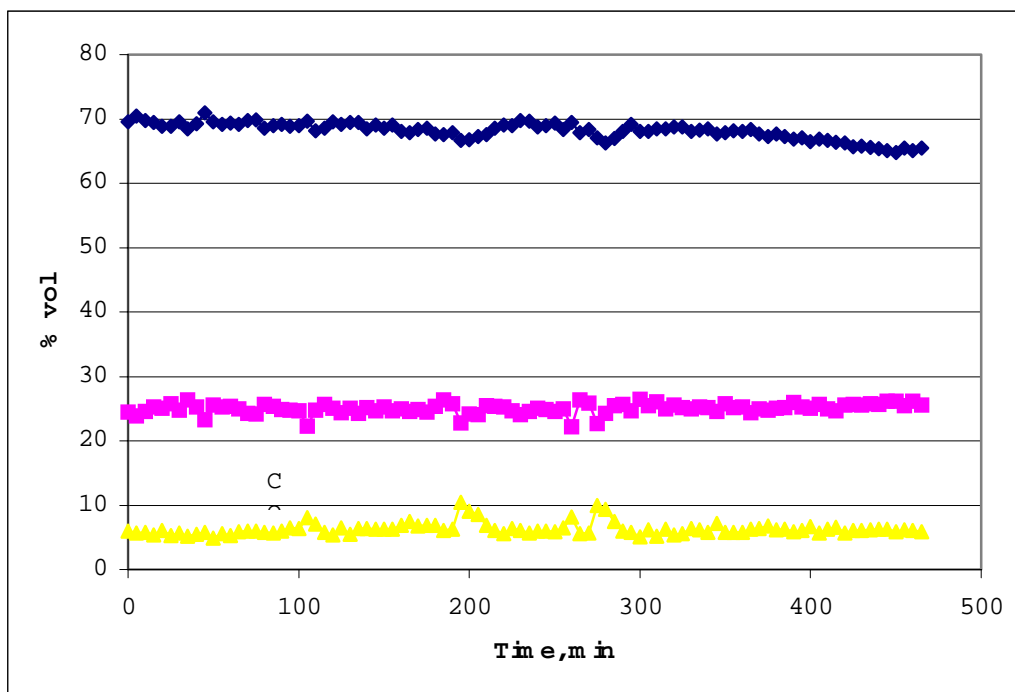

Figure 3. Composition of the gas produced during steam reforming of peanut shell bio-oil carbohydrate-derived fraction at 850°C and S/C=9 [3].
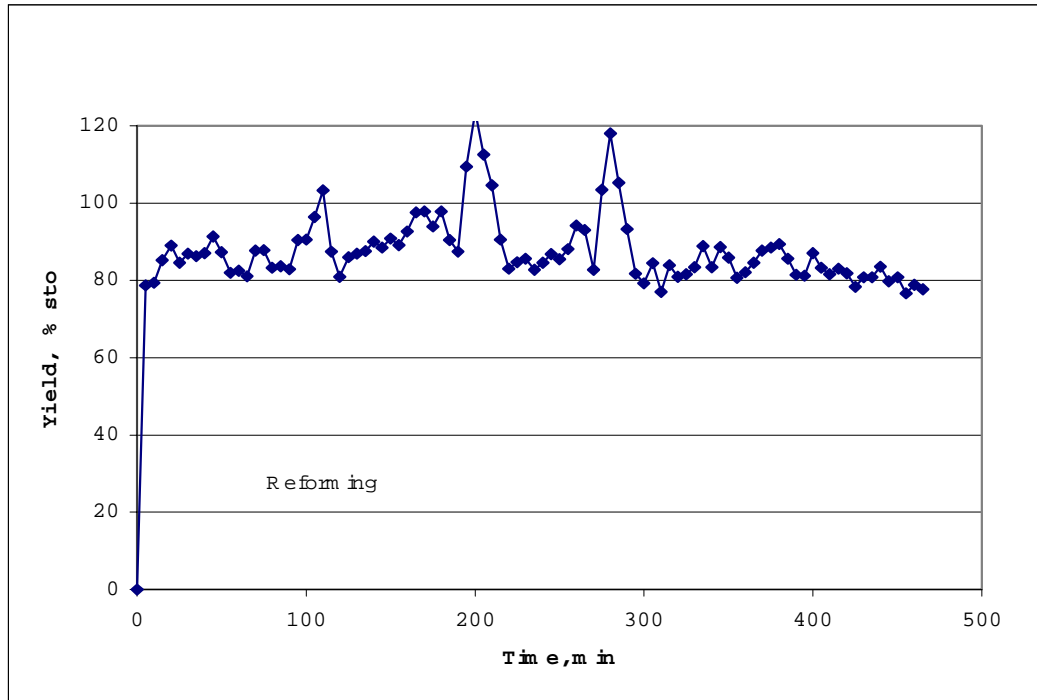
Figure 4. Yield of hydrogen obtained during reforming of peanut shell bio-oil carbohydrate-derived fraction at 850°C and S/C=9 [3].

Process Economics

The work performed at NREL to date has focused on the scenario shown in Figure 1 for fast pyrolysis. The economics of this approach has been assessed with an adhesive coproduct and the selling price of hydrogen is estimated in the range of $6-8/MBTU [4]. This study addresses another process option based on slow pyrolysis, which is currently practiced to produce charcoal for conversion to activated carbon. A modification of this approach to convert the by-products to hydrogen is shown in Figure 5. A preliminary economic analysis of the steam reforming of the bio-oil produced from the activated carbon process has been performed by NREL [5,6]. The process examined included steam reforming of the slow pyrolysis vapors, followed by further hydrogen production in shift reactors and hydrogen purification in a conventional pressure swing adsorption (PSA) system. The base case process assumes utilization of all of the 225 kg of pyrolysis vapors/hr (the current scale of the Scientific Carbons process). At this utilization rate, it appears that the carbon process is still slightly positive with respect to energy, although this will depend on heat losses. In other words, the process produces enough energy to sustain the system without requiring additional fuel.

The yield of hydrogen from the slow pyrolysis bio-oil is significantly higher (~70%) on a mass basis than that from the fast pyrolysis bio-oil. When looking at the total process (i.e., biomass to bio-oil to hydrogen), however, the yield from the slow pyrolysis process is lower than that from the fast pyrolysis process. Table 1 compares the yields from both processes. As shown in Table 1, the yield of hydrogen from bio-oil in the fast pyrolysis system is roughly 11%, but in the slow

pyrolysis case, it is almost 19%.   However, the yield on a total dry biomass basis is 4.5% for slow pyrolysis and 7.3% for fast pyrolysis.   The primary reasons for these differences are variations in the bio-oil composition, yield of other products, and process assumptions.

Also shown in Table 1 are estimates of the composition of the bio-oil from both processes. In the fast pyrolysis process, the bio-oil has a composition that is < 50% carbon, but that from the slow pyrolysis process has a carbon composition of almost 73% [5]. Thus, for the same steam addition rate (i.e., lb H_2O/lb C), more hydrogen will be produced per pound of bio-oil in the slow pyrolysis process.
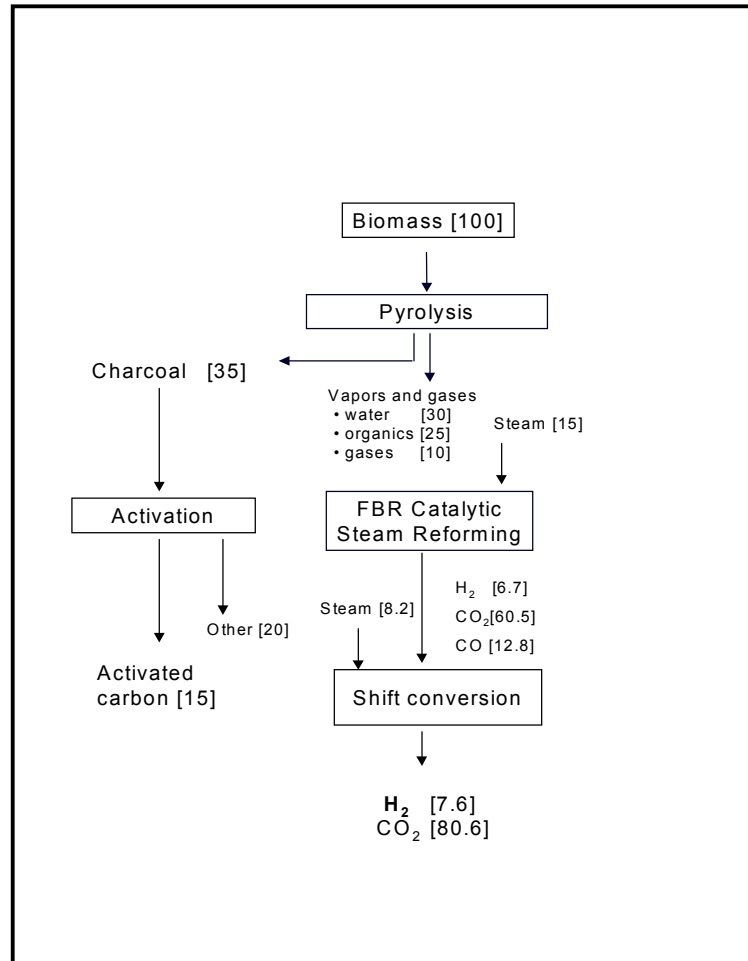

Figure 5. Proposed process based on reforming of slow pyrolysis oils.

The economic feasibility determination was based on a discounted-cash-flow rate of return (DCFROR) analysis using a 10% rate of return. All parameters for the study were taken from the standardized hydrogen economic analysis [6]. Table 2 summarizes the important economic parameters.

Table 1. Yield Comparison for Slow and Fast Pyrolysis

Process	Slow Pyrolysis	Fast Pyrolysis
Bio-oil Yield (kg/kg dry feed)	0.239	0.657
Hydrogen Yield		
(kg/kg dry feed)	0.045	0.073
(kg/kg bio-oil)	0.189	0.111
(kg/kg vapor)	0.063	NA
(kg/kg dry vapor)	0.113	NA
Bio-Oil Ultimate Analysis (wt%)		
Carbon	72.50	48.71
Hydrogen	5.13	6.61
Nitrogen	1.2	0.0
Sulfur	0.04	0.0
Oxygen	21.13	44.68

NA – Not applicable; the vapors are not processed in the fast pyrolysis process

Table 2. Standard Economic Parameters

Economic Parameter	Value
Discount rate	10%
Plant life	20 years
Depreciation	None
Construction Period	3 years
On-stream time	Year 1 45% Year 2+ 90%

Capital costs were scaled from Mann [4] using a 0.84 exponent. This exponent was derived from the three cases presented in the paper [4]. Fixed operating costs and working capital were also based on the paper. Variable operating costs were determined from the material balance. The pyrolysis vapor was assumed to be available at $2.56/GJ, a value that is roughly 90% of its fuel value (assuming an energy equivalence to natural gas at $2.50/GJ). The analysis also assumed that steam would be produced in the reforming operation. A credit based on $3.50/1000 lbs of steam was assumed.

Using the above assumptions, the total capital investment for the additional equipment to modify the existing facility to produce hydrogen from the pyrolysis off-gas is estimated at $1.4 million. For an annual hydrogen production rate of 4.4 million Nm^3, the selling price of hydrogen is estimated to be $9.51/GJ. The hydrogen-selling price for a fuel cost of $1.28/GJ (i.e., 45% fuel value) is $7.78/GJ. Using a no-cost bio-oil the selling price for the hydrogen is $6.05/GJ. These price ranges are very promising considering that the economics were performed for a very small-scale operation.

Advantages and Potential Impact

The proposed method combines two stages: pyrolysis of biomass to generate bio-oil and catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide. This concept has several

advantages over traditional gasification technology. First, bio-oil is much easier to transport than solid biomass and therefore, pyrolysis and reforming can be carried out at different locations to improve the economics. For instance, a series of small size pyrolysis units could be constructed at sites where low cost feedstock is available. The oil would then be transported to a central reforming plant located at a site with an existing hydrogen storage and distribution infrastructure. A second advantage is the potential production and recovery of higher value added co-products from bio-oil that could significantly impact the economics of the entire process. In the original NREL concept, the preferred route leads to co-products hydrogen and partly "depolymerized lignin." Lignin-derived oligomer-rich fraction can be used as a feedstock for the production of resins with formaldehyde. Such resins can become valuable co-products (a substitute for phenol-formaldehyde), which will lower the production costs of hydrogen from the aqueous fraction as demonstrated in related technoeconomic studies [4]. Other viable application of the lignin-derived fraction is the production of "oxyaromatic ethers," a new class of high-octane fuel additive. The economics of the whole bio-oil reforming are less favorable than for the co-product strategy. However, the hydrogen yields obtained from the whole oil are higher than in the case when only the aqueous, carbohydrate-derived fraction is processed. In addition, since hydrogen is the only product, this option is independent of co-product markets.

A key partnership that will be fostered in this project is with the Federation of Southern Cooperatives, an organization of southern family farmers that represent 25,000 farmers in a 13-state region. As part of the assessment for expanded application of this technology, we will develop a database of the biomass and agricultural residues (and their volumes) that may be used as potential feedstocks in the proposed conversion scheme. The information from the database will be used to assess the economic and environmental impact of the proposed work on the state of Georgia.

The anticipated potential benefits or impact on the Georgia economy include:
- Use of biomass will support and further expand the agriculture-related sector, which is the largest industry in Georgia; employing one in six Georgians and producing 45% of the U.S. peanut production.
- Application of the proposed technology will provide an economical and environmentally acceptable means of disposing of the large quantity of peanut shells that result from the 1.5 billion pounds (768,500 tons) of peanut produced each year in Georgia. The demand for peanut shells as feedstock of the proposed technology will improve the economic competitiveness of the peanut industry in Georgia and secure its long-term future.
- Widespread use of renewable hydrogen, the cleanest fuel for power generation and for transportation applications, will reduce oil and gas imports and will have significant environmental and health benefits for the major cities in the state of Georgia.
- The proposed process will produce co-products in addition to hydrogen. Alternative co-products that may be obtained from different bio-oil fractions include phenol (for phenol-formaldehyde resins) and fuel oxygenates. Similar to petroleum crude oil, biomass pyrolysis oil can be used for the production of a multitude of fuel and chemical products, in addition to hydrogen.
- The development of new agro-industrial infrastructure options that could result in sustainable and equitable growth. The inclusion of small farms and the attention to the appropriate scale

of production technology will ensure the ability to distribute the benefits of enhanced materials along the value chain to the communities involved in generating the wealth.

Approach and Accomplishments

Feedstock Supply, Process Economics, and Deployment Strategy

The ultimate impact of the biomass-to-hydrogen process depends on overall economics. Feedstock issues, such as supply, cost and logistics are major factors in cost-effectiveness of the hydrogen production process. This task is developing decision models for selecting among feedstock, process, and deployment alternatives. Of particular interest in Phase 1 on this project are peanut shells supply and cost projections and the evaluation of other agricultural residue feedstocks available in the same geographical area. Process economics are being developed for the major process options and used to construct a process options database. Different network options are developed to determine optimum subdivision of tasks among potential sites and to develop criteria for location of new processing sites. The evaluation of other coproducts are also included. This work is utilizing Geographical Information Systems (GIS) databases for constructing various scenarios relative to feedstock location, plant location and hydrogen and co-product markets.

Process Modeling

The current process converts peanut hulls into activated carbon and derives a bio-oil for fuel via pyrolysis. The process modeling effort is directed towards evaluating the enhancement of this basic process with options to recover a phenolic fraction for further processing into adhesives and steam reforming and hydrogen purification for a transportation fuel. The main unit operations that can achieve this separation and further refining are liquid-liquid extraction (LLE), steam reforming and pressure swing absorption (PSA). Three alternative flowsheets for the process are shown in Figures 6, 7 and 8. To model the LLE process it is necessary to establish the solubility of various components of the bio-oil in water and organic solvents. To achieve this goal it is necessary to characterize and model the bio-oil that is generated from the pyrolysis process and to ensure that the phase behavior of the components is adequately described in the process simulator. The description of the bio-oil components has been the main focus of the effort in process modeling at this stage. We have tried to identify key component classes, and representative components within these classes that can be used to test the ability of the process simulator to match the phase behavior of the components.

Prior to developing a model for simulating the processing of biomass derived pyrolysis oils, an attempt to characterize these oils was undertaken. This course of action involved both a survey of the existing literature to identify compounds prevalent in pyrolysis oils, as well as an attempt to use HYSYS, a process simulator package from Hyprotech, to simulate a typical process oil with a few representative compounds for further analysis.
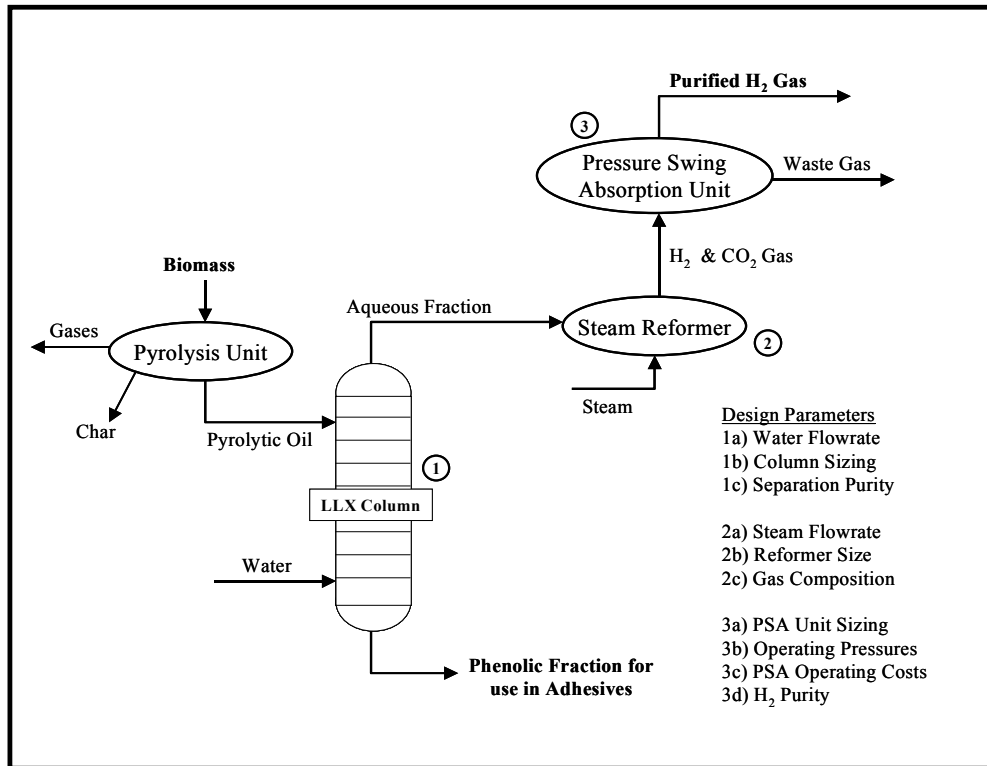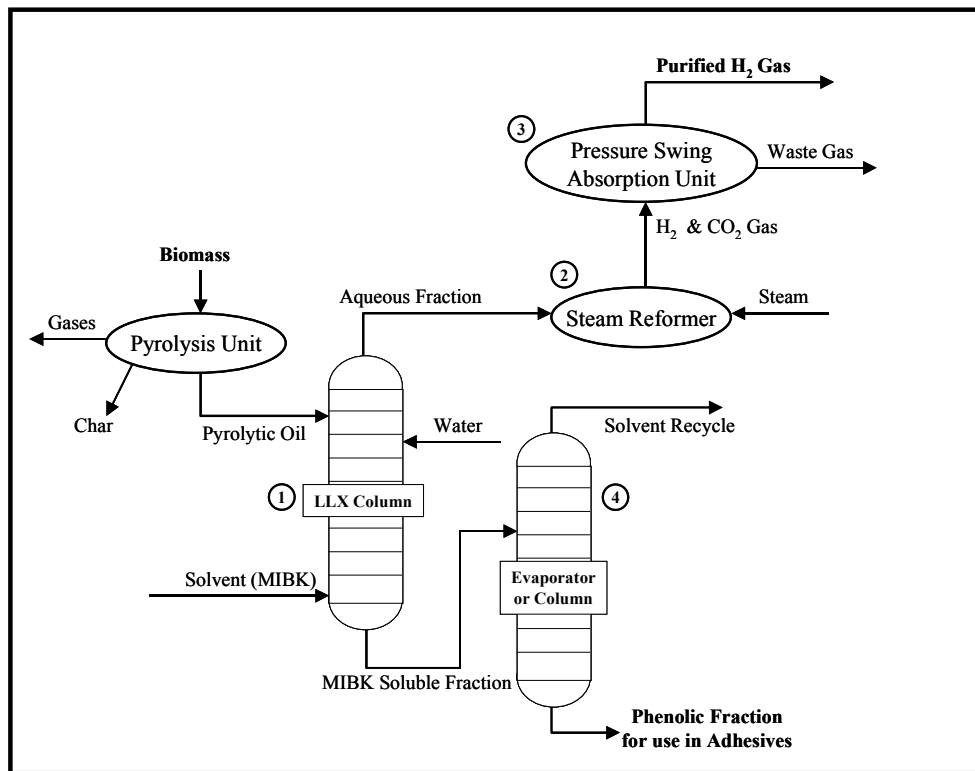
Figure 6. Stage Aqueous Extraction

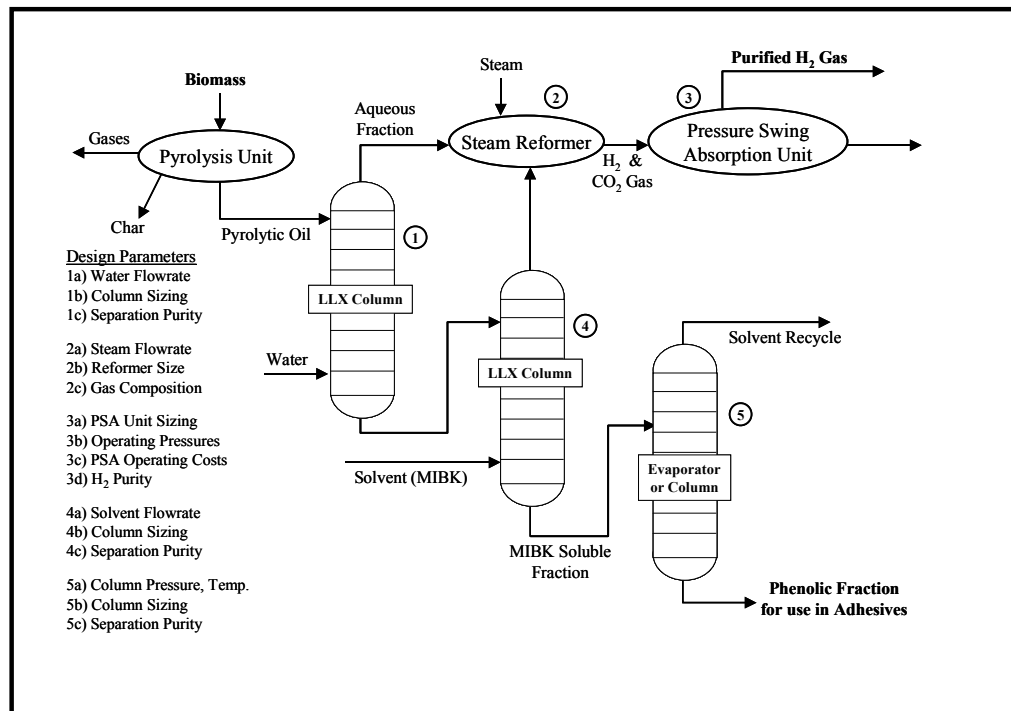**Figure 7.** Stage Simultaneous Extraction

Figure 8. Stage Extraction

In general, the range and variety of chemicals found in pyrolysis oils shown in Table 3, far exceed that of crude oil to which analogies are often drawn. The key difference between bio-oil and crude oil is the prevalence of oxygenated compounds in bio-oil as opposed to fully reduced hydrocarbons in crude oil. However, some trends can still be noted due to the shared biological components common to the majority of plant life from which many pyrolysis oils are derived. In particular, the presence of cellulose and other polysaccharides causes the formation of various carbohydrates in the oils. Similarly, the several types of lignin found in "woody" biomass sources form the basis for most phenolic and aromatic compounds found in pyrolytic liquids [7]. The phenolic compounds are of particular interest and present one of the more feasible economic opportunities for development in the form of phenol based-adhesives. Developing a realistic process model hinges not only on the composition of the phenols present but also on the other various carbohydrates, acids, alcohols and other compounds present in large quantity which must be separated out and directed to the highest value end uses.

In general, the distribution of chemicals in the oil depends not only on the compounds found in the biomass but also on the pyrolysis operating conditions (residence time, temperature, pressure, and type of reactor). To date, no systematic compositional analysis has been undertaken for a large number of compounds at reproducible operating conditions. This situation can be attributed to the large number of possible feedstocks, the interest in particular feedstocks to the exclusion of others being influenced strongly by geographic region and industry, and the early stage of development that exists for bio-oil processing. Development that has been done to date has focused heavily on the processing of wastes associated with the forestry industry [8]. An attempt

has been made to compile a list of compounds common to pyrolysis oils from varying sources in order to create a characteristic bio-oil of "typical" composition.

Table 3. Pyrolysis Oil Composition [8-10]

Acids	Aldehydes	Syringols
formic (methanoic)	methanal (formaldehyde)	syringol (2,6-dimethoxy phenol)
acetic (ethanoic)	ethanal (acetaldehyde)	methyl syringol
propanoic	2-methyl-2-butenal	4-ethyl syringol
hydroxyacetic	**Phenols**	syringaldehyde
butanoic	phenol	4-prophenyl syringol
pentanoic	2-methyl phenol o (o-cresol)	4-hydroxy-3,5-dimethoxyphenylethanone
4-oxopentanoic	3-methyl phenol m (m-cresol)	**Mixed Oxygenates**
hexanoic	4-methyl phenol p (p-cresol)	glyoxal
benzoic	2,3-dimethylphenol (2,3-xylenol)	Methylglyoxal
heptanoic	2,4-dimethylphenol (2,4-xylenol)	hydroxyethanal
dodecanoic acid	2,5-dimethylphenol (2,5-xylenol)	1,2-dihydroxyethane
Sugars	2,6-dimethylphenol (2,6-xylenol)	propanal-2-one
o-xylose	2-ethylphenol	1-hydroxy-2-propanone
1,6-anhydroglucofuranose	2,3,5-trimethylphenol	2-hydroxypropanal
levoglucosan	**Guaiacols**	butyrolactone
alpha-D-glucose	guaiacol (2-methoxyphenol)	2,3-pentenedione
fructose	4-methyl guaiacol	1,2-dihydroxybenzene
cellobiosan	4-ethyl guaiacol	1,3-dihydroxybenzene (rescorcinol)
glucose	4-prophenyl guaiacol	1,4-dihydroxybenzene
mother oligosaccharides	eugenol	2-hydroxy-3-methyl-2-cyclopentene-1-one
Alcohols	isopugenol	methylcyclopentenonone
methanol	4-propyl guaiacol	2-methyl-3-hydroxy-2-pyrone
ethanol	**Ketones**	hydroxyacetaldehyde
cyclohexanol	2-butenone	4-hydroxy-3-methoxybenzaldehyde
Furans	2-butanone (MEK)	Testosterone
furan	cyclopentanone	Methyl Salicate
2-methylfuran	3-methyl-2-cyclopenten-1-one	Ethylene glycol
2-furanone	2-ethylcyclopentanone	Acetol
furfural (2-furaldehyde)	dimethylcyclopentanone	Acetoin
3-methyl-2(3H) furanone	trimethylcyclopentanone	pyrolytic lignin (water insoluble)
6-methyl furfural		Various tannins
6-hydroxymethyl-2-furaldehyde		Various flavonoids
1,6 anhydroglucofuranose		

From this table of compounds, a select list was developed and is shown in Table 4, that represents both the major classes of compounds, present in typical ratios as well as C/H/O molecule ratios desired for the subsequent process model that will be developed. At this time, the select list of compounds contains the following chemicals:

Table 4. Representative Compounds of Bio-oil for Process Simulation

Representative Compounds	
water	phenol
ethanol	2-methyl phenol (o-cresol)
methanol	2-butanone
cyclohexanol	dodecanoic acid
formic Acid	hypothetical steroid
acetic Acid	hypothetical flavonoid
glucose	hypothetical tannin

The distributions of the compounds are varied based upon the predicted C/H/O ratios for a particular situation within the constraint of reported compound distributions from literature sources. Additionally, total phenolic content is varied but kept near or below the composition of 55 wt%, an achievable value with modern pyrolysis techniques focused specifically on phenolic specific liquid production [9].

Logistics & Overall System Design

The basic goal of this part of the project is to determine the overall system information for evaluating widespread adoption of peanut or other sources of biomass for value-added processing. This required two subtasks. The first is finding specific information for peanut hulls, some of which is summarized below, and some of which is provided in the form of maps showing the distribution of peanut production in southeastern USA. The second is to develop a more generic analysis of the interaction of collection of biomass and the scaling of process cost.

Our current understanding of the southeast region peanut hull market is summarized as follows. Peanut hulls are not traded as a commodity as are peanuts. Hull prices are not reported publicly and are set by the few players (primarily Birdsong and Golden's hull marketing arm). Moreover, these sellers have a large storage capacity so the price and supply of hulls are neither highly seasonal, nor highly correlated with the price or supply of peanuts. There are two major sellers in the southeast, Golden (#1) and Birdsong (#2) and this industry is quite concentrated. Birdsong has 5 plants in the southeast (not including Virginia).

Peanuts are about 20% hulls by weight, and this is a little variable, maybe ranging from 20-22%. Hull density is ~9-10 lb/ft³. Shells are sold in three major forms: loose (unprocessed), ground, and ground then pelletized. Current prices are about $10-20/ton loose and $40/ton pelletized, with purchasers generally paying for transport. The hull market is relatively new. New uses for hulls are continuing to arise, causing the price to trend upward. Uses for hulls include: livestock feed, chicken litter, insulation board, metal casting, a medium for pesticides, as well as activated carbon.

While projecting hull prices is difficult due to the market structure, the overall supply of peanuts can be projected based on projections for peanut supply---hulls comprise about 20% by weight of unshelled peanuts. Future prices will likely depend on the development of new uses for hulls and the prices of substitutes for the various uses. Prices are trending up due to increasing demand, as more new uses for hulls are developed. This is a bad combination with the prices for activated carbon possibly trending down, though none of the uses is very high-value, and most have other relatively cheap substitutes. A ceiling on the long-term price of hulls is probably low, but not yet determined.

Facility Location/Allocation Models for Process Scale & Transportation Tradeoffs

The most economically efficient sizing and location for biomass processing facility depend in large part on the geographic availability of the feedstock and raises important issues in the trade-offs between economies of scale to be gained from large processing facilities and the diseconomies of scale for agricultural inputs.

These issues are not yet well addressed in the literature. We are working to understand the relationship between the geographic availability of feedstocks (perhaps peanut hulls) and the optimal number and size of processing facilities, to narrow the parameters for facility location and process design.

Biomass processing is for the moment a low-revenue business. To be economically feasible, it must also be low-cost. Its cost structure is unusual in a few specific ways, most notably, because the overall costs must be low. Additionally, because the inputs to the process are agricultural products, they arise from highly distributed sources, and so the material transportation costs contribute significantly to overall costs. This cost structure can also occur in distribution systems to customers and in reverse logistics systems, e.g. for collecting end-of-life products for recycling or remanufacture.

The literature on facility sizing does not usually account for input transportation costs---the unit prices of inputs are usually assumed to be constant regardless of the quantity demanded by each facility. This does not hold true, however, when additional units of inputs must be transported from larger and larger distances.

The literature on facility location and allocation of capacity, on the other hand, does not usually include explicit consideration of facility costs as a function of either capacity or throughput. Perhaps because sizing decisions are made upstream, without reference to input transportation costs, the facility location/allocation problem is often to locate a given number of new facilities, among existing facilities. Using assumptions that are unrealistic for our application, Love et al [11], shows curves similar to those shown for the "elegant" model, for finding the optimal number of facilities. It is also usually assumed that input sources and output sinks are fixed points. Moreover, the models used in transportation are usually very detail-heavy and specific, making it hard to draw any general conclusions about optimal facility sizing, for example.

When the models in the existing literature on the economics of biomass processing do attempt to quantify transportation costs, they use very location- and application-specific models, often using GIS models, taking destinations as given (does not optimize with respect to location) and their results cannot be generalized. While many of the economic models for biomass processing do not take transportation into account at all, those that do often find it to be a significant contributor to total costs:

- Angus-Hankin et al [12] 20-40% delivered input cost
- Nilsson [13] ~30%
- Gomes et al [14] $.14-.21/km-ton vs. total delivered price $18.04-38.23/ton

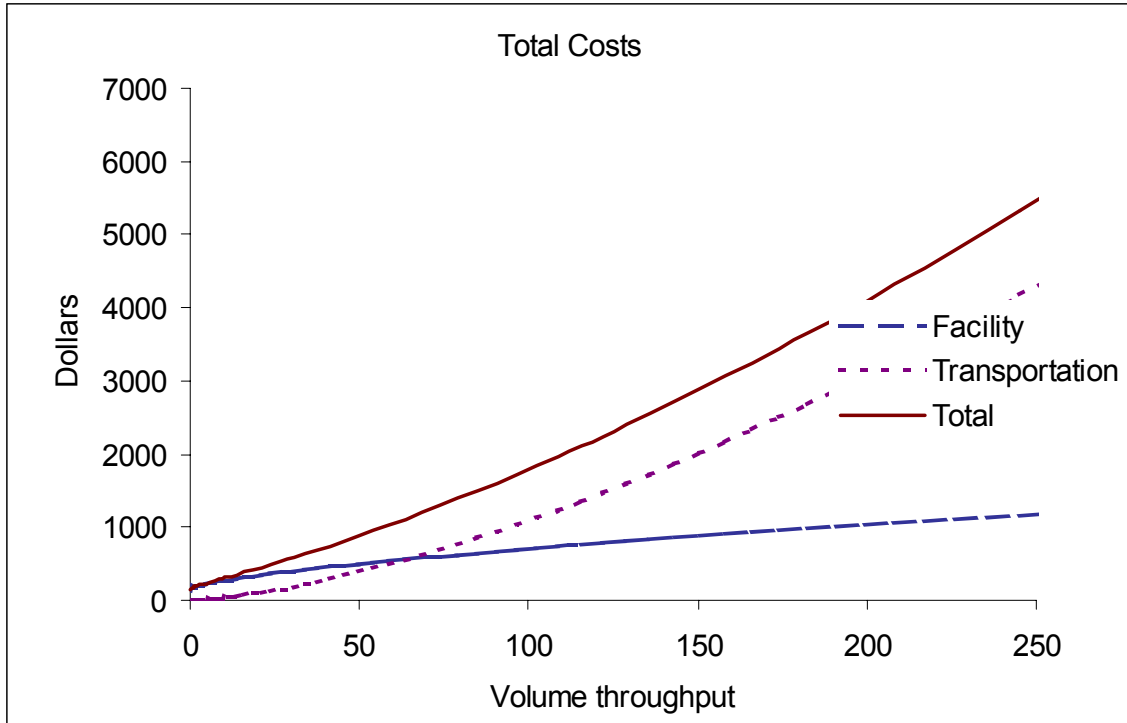Figures 9 and 10 show some of the model/simulation predictions.

Figure 9. Sample model/simulation prediction of total cost vs. volume throughput.
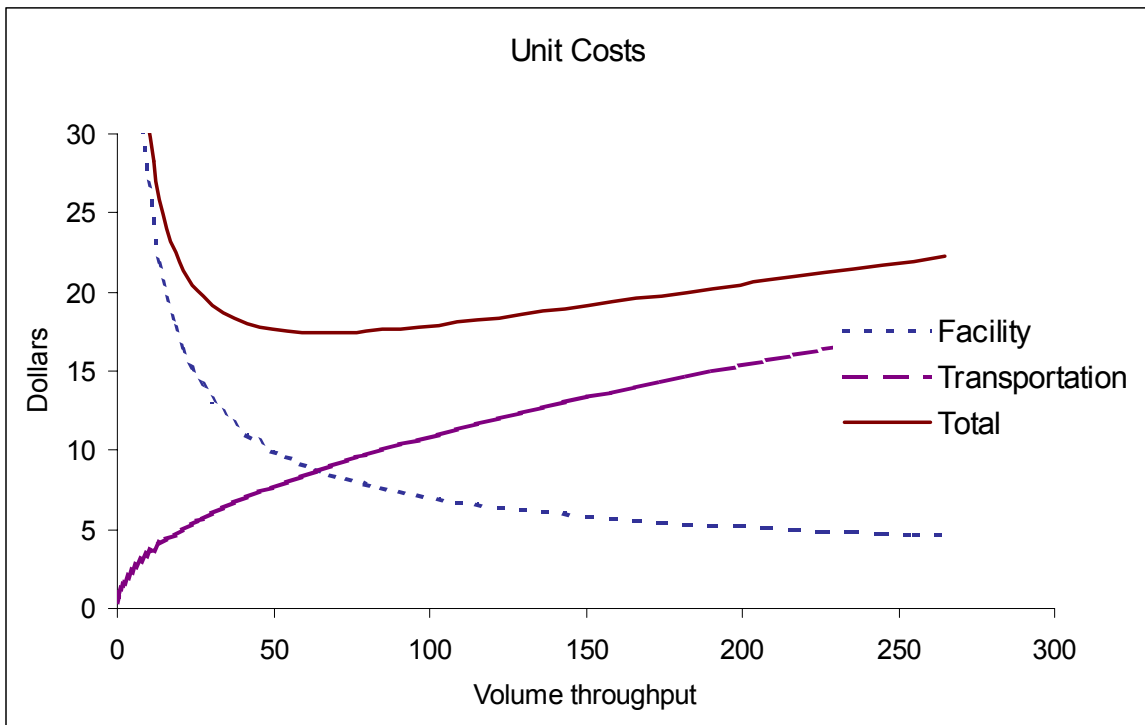

Figure 10. Sample model/simulation prediction of total cost vs. volume throughput.

Reactor Development and Commissioning: Design, Construction and Shake Down of a Catalytic Fluid Bed Reformer Capable of Processing 10-20 kg/h of Pyrolysis Vapors.

The catalytic fluid bed reformer was designed and constructed based on past results with the bench-scale, fluid-bed reactor. The schematic of the reformer is shown in Figure 11. The reactor can process 7-10 kg/h of pyrolysis vapor. The maximum allowable operating temperature and pressure are 900° C and 140 kPa, respectively. The reformer is equipped with fluid bed reactor, vapor and liquid injection, steam (and O_2) injection, internal and external cyclones for disengaging catalyst particles, heat exchanger to recover heat and condense the water vapor, instrumentation, data acquisition, and safety features (alarms, etc.). The product collection line includes a cyclone that captures fine catalyst particles and possibly, char generated in the process and two heat exchangers to condense excess steam. The Inconel reactor with a porous material distribution plate is placed inside a three zone electric furnace. Commercial nickel-based catalyst ground to particle size 300-500 μ is used in the reactor. The catalyst is fluidized using superheated steam, which is also a reactant in the reforming process. The initial shakedown of the reactor is being performed at NREL's TCUF.
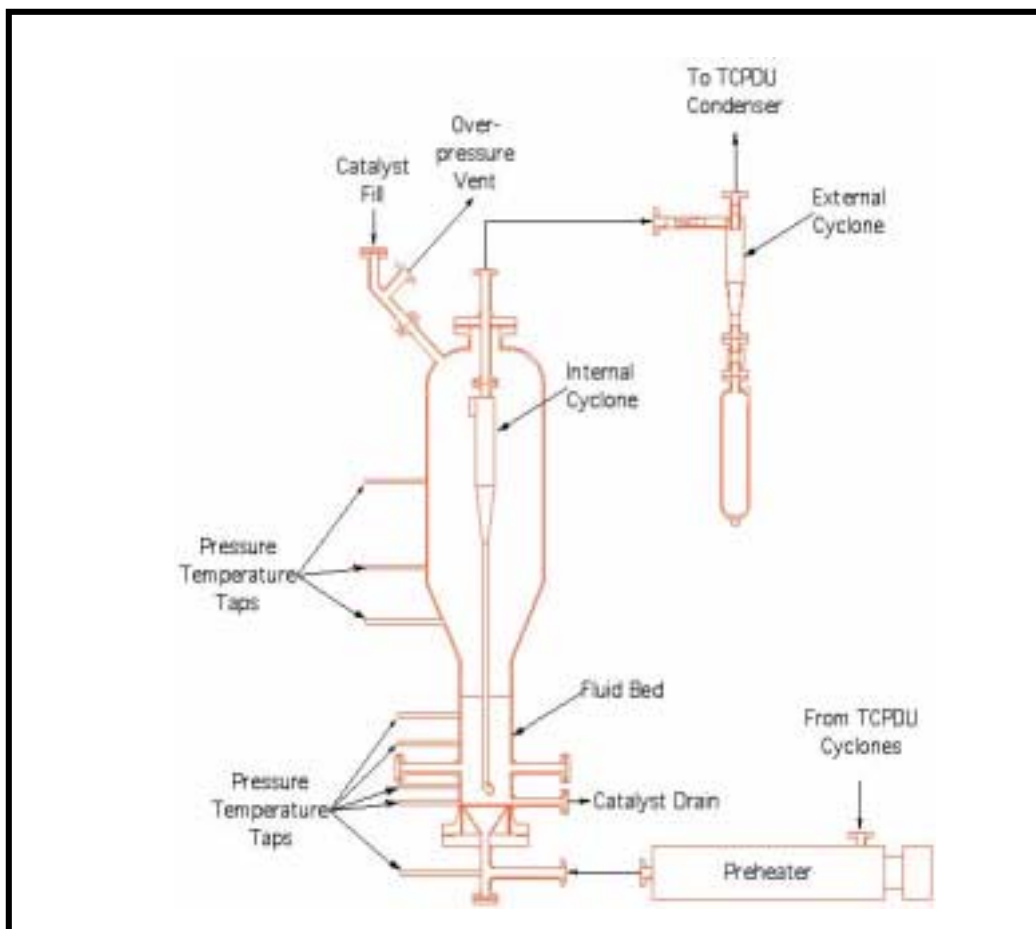

Figure 11. Schematic of the fluid bed reformer

For the initial runs, a commercial nickel-based catalysts from UCI is being fluidized using superheated steam which serves as a reactant in the reforming process. A 10-20 kg/hr fluid bed pyrolysis unit at TCUF is able to feed the steam-reforming unit for the shakedown. The steam reforming reactor system was shipped to NREL in March 2001 and installed in April 2001. Two tons of pelletized peanut shells were shipped from Scientific Carbons to NREL for the tests. The catalyst, in a form suitable for fluid bed, is not commercially available and hence has been purchased from United Catalysts. Initial tests are monitoring catalyst fluidization and attrition under simulated conditions. Methane reforming is being used to verify catalyst performance. Subsequent runs with pyrolysis vapors will be performed until performance matches previous work at the bench scale.

The process conditions and description for the hydrogen reformer system are as follows:

Process Conditions
Maximum Temp: 900° C (1650˚ F)
Maximum Pressure: 140 kPa (20 psig)

Process Gas Composition
Steam: 16 kg/hr (35 lb/hr)
Hydrogen: 1.2 kg/hr (2.6 lb/hr)
CO_2: 14 kg/hr (31 lb/hr)
CO: 1 kg/hr (2.2 lb/hr)

Description of Reformer Vessel
Vertical Reformer Vessel (Figures 12 and 13)
- Constructed entirely of Alloy 800 except for the exterior flanges.
- Exterior flanges N1 and the bottom closure is 316 stainless overlaid with Alloy 800. Other exterior flanges are 316 stainless steel.
- A Carbon steel support structure with the approximate dimensions of 52" wide and long and 64" tall and painted with a high temp coating system.
- External cyclone and the catch vessel are also constructed as the same materials as the reformer vessel and includes:
- A high temp ball valve is located between the external cyclone and the collection vessel.

The reformer vessel, the external cyclone and its catch vessel are designed, fabricated, inspected, tested and stamped in accordance with the *ASME Boiler and Pressure Vessel Code, Section VIII, Division 1, 1198 Edition,* for 20 psig at 1650°F with no corrosion allowance.

Preheater Vessel
- 3" pipe size x 59" overall length circulation preheater with 1.5" class 300 flanged inlet and outlet connections and mounting supports for horizontal mounting
- Vessel fabrication of 316H stainless steel.
- Three tubular heating elements sheathed in Inconel 600 and designed for operation at 240 volts a.c, 4 kW maximum.
- NEMA 4 terminal housing

- Hi-Limit type K thermocouple is attached to the vessel shell and Process type K thermocouple is located near the outlet.
- The preheater vessel is thermally insulated with 2" TR-19 insulation and two 2" layers of Calcium Silicate insulation
- The preheater vessel was designed, fabricated, inspected, tested and stamped in accordance with the *ASME Boiler and Pressure Vessel Code, Section VIII, Division 1, 1198 Edition,* for 50 psig at 1450°F with no corrosion allowance.

Thermal Contact Protection
- The preheater vessel, reformer vessel, external cyclone (Figure 14) and the catch vessel are provided with insulation and/or external guarding to prevent accidental human contact with surfaces having a temperature greater than 150° F during normal operation.
- The carbon steel support structure for the vessel provides support for the preheater vessel and ceramic wool insulation with a further covering of expanded metal.

Reactor Vessel Heaters for Section 1, 2, and 3
- 2-piece, semi-cone shaped ceramic fiber heater
- Dimensions are 26" inside diameter x 36" section 1; 18" inside diameter x 14.25" long for section 2, and 12" inside diameter x 27.5" long for section 3
- Designed for operation at 240 volts a.c.

Control Panel for Preheater and Reformer Heaters
- As designed and built by Watlow Heaters
- 56 kW, three phase
- Four Watlow Din-A-Mite power controllers
- Four Watlow Series F4 Process Controls with cascade software
- Four Watlow Series 146 Hi-Limit Devices for over temperature protection
- On / Off / Set up Control selector switch with pilot light
- Hi-limit pilot lights with common reset pushbutton
- Mounted in a 36" high x 24" wide x 10" deep NEMA 12 electrical enclosure with filtered cooling fans
- Controls wired and tested at Watlow factory

The above reformer system, designed by the project team, was constructed by an outside professional firm through subcontracting. A photograph of the final product is shown in Figure 15.
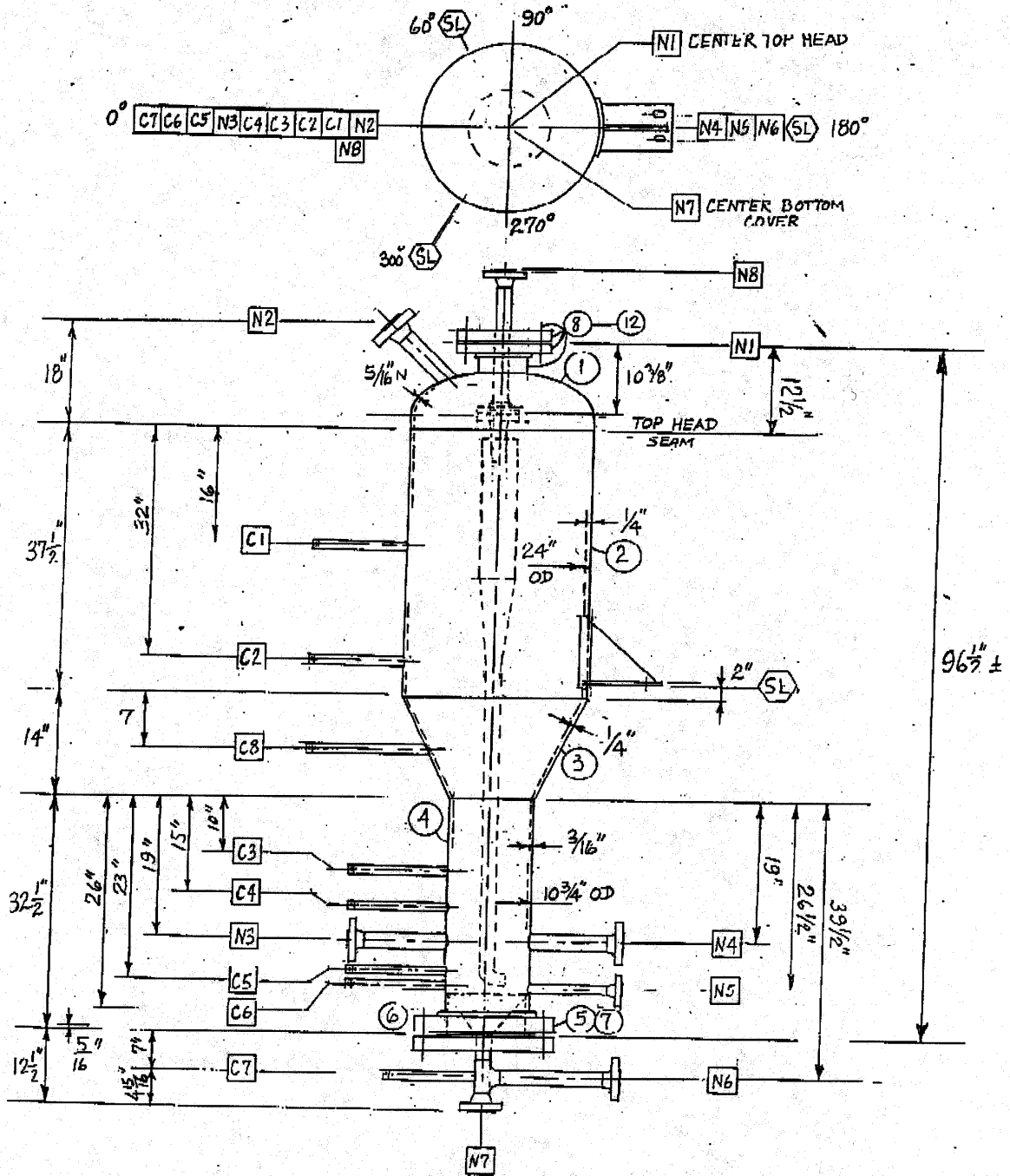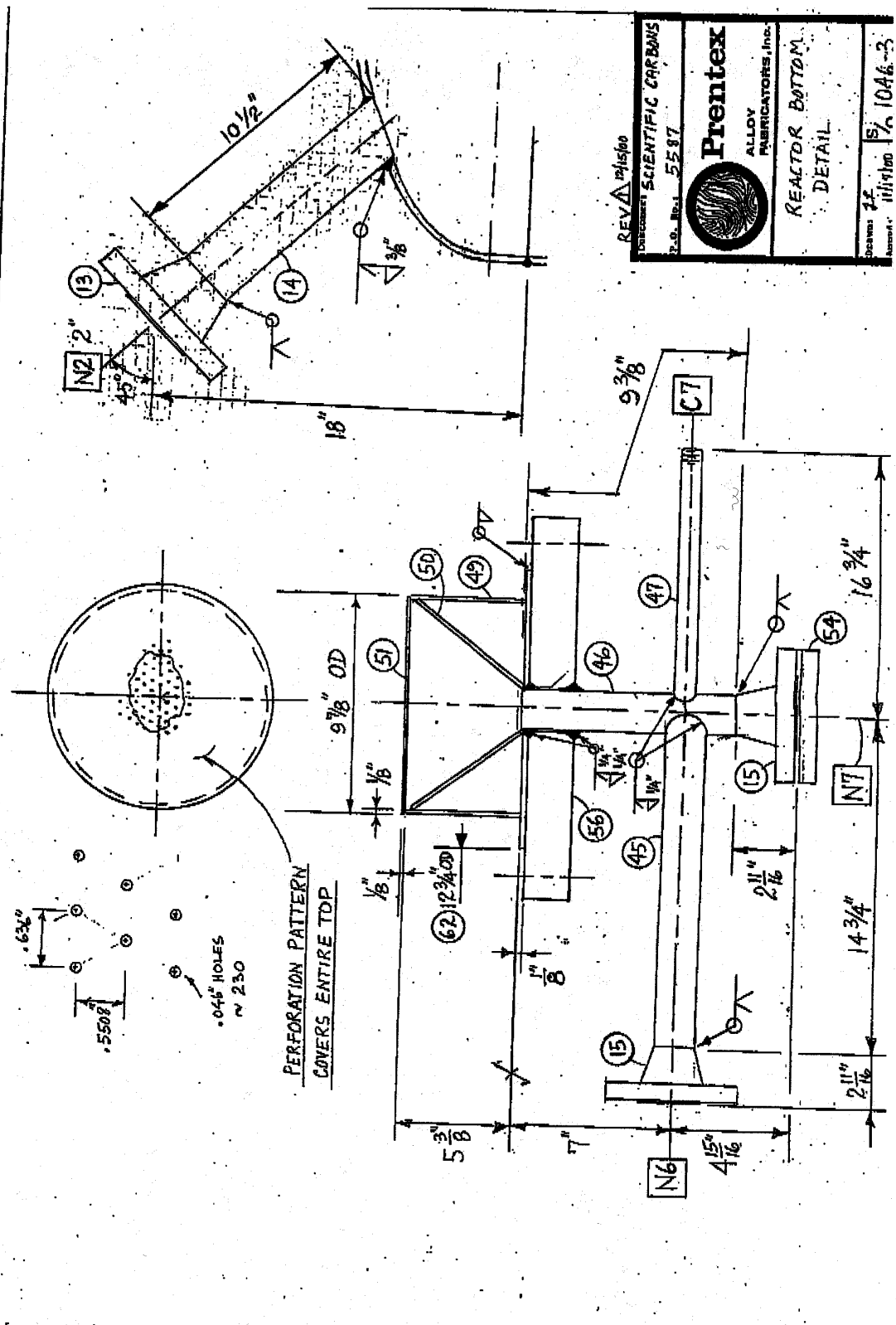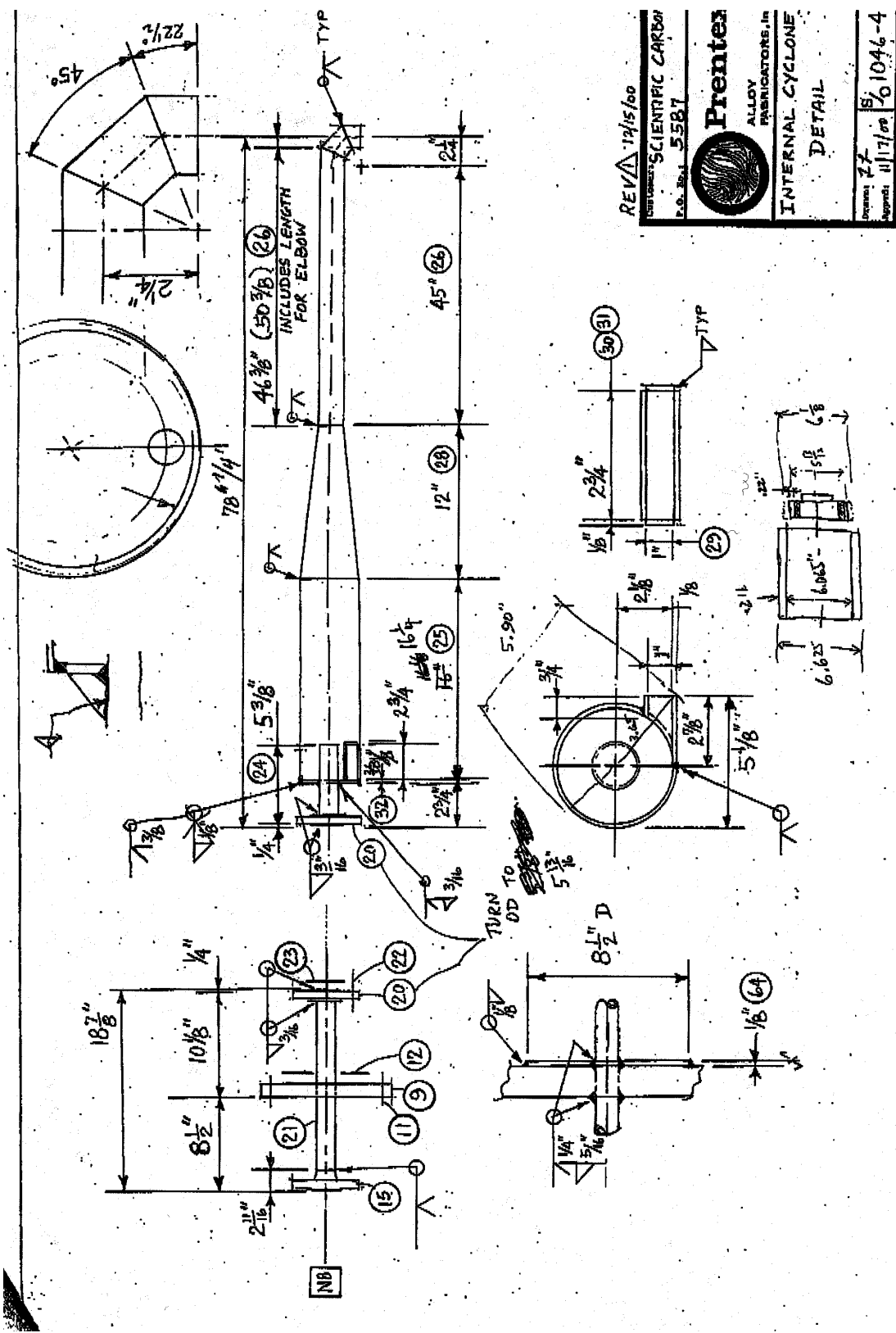
Figure 12. Vertical Reformer Vessel

Figure 13. Reactor Bottom Detail

Figure 14. Internal Cyclone Detail

Figure 15. Fluidized-bed catalytic reactor

Preparation for long-term testing at Scientific Carbons.

Work has begun on the location of the interface and the operating conditions. An assessment is being made of the impact of the long-term steam reforming tests on the mass and energy balance of the current Scientific Carbons operation. The existing pyrolysis facility owned and operated by Scientific Carbons, will be modified as follows:

- Design, construction and addition of a slip stream capable of withdrawing 10-20 kg/h of pyrolysis vapors
- Installation of instrumentation and on-line monitoring and data acquisition for the above system for product stream analysis, and process mass and energy balance.

The operation of the system at the Scientific Carbons Inc. site will not occur in Phase 1, but would begin in the second year under a Phase 2 project. We have prepared the necessary analytical systems to monitor the transportation system performance.

Preparation for Hydrogen Storage and Utilization

We have begun analysis of how storage will be accomplished on the Scientific Carbons site. Past approaches to the storage of hydrogen in mixtures with compressed natural gas are being reviewed and calculation of mixture limits are being made. Other storage options are being explored that will meet the needs of the planned demonstration. Model system testing will be performed. The design of a storage system is being done and include:

- Pressure Swing Absorption (PSA) system for the purification of hydrogen and the separation of CO_2
- Holding tank (or another device) for H_2 storage
- Compression station to charge the H_2 into blends with CNG
- Instrumentation and on-line monitoring and data acquisition for the above system

In preparation for hydrogen utilization, our activities in Phase 1 have included identifying the community partner and working with that partner to define the transportation fleet application. The utilization system design will then occur including modification to a refueling station and the vehicle(s). Up to 30% of hydrogen by volume could be stored in this way and hence the blend would enable the hydrogen produced to be used in a convectional CNG bus without major modifications. To simplify the start up of the project, the system would begin with commercial sources of hydrogen.

Environmental and Technical Evaluation

An important part of the decision to implement a hydrogen transportation technology will be documentation and evaluation of benefits and system performance. We have begun this evaluation in conjunction with the planning of the bus demonstration.

Partnership Building and Outreach

We coordinated the fuel utilization demonstration by working with a local municipality to operate a vehicle, such as a transit bus, under normal operation. Work has begun with local parties to participate in the transportation demonstration. We have received a letter of interest in accepting partnership role from Albany State University (ASU) to host the hydrogen bus demonstration in the city of Albany Georgia. Albany Water, Gas & Light Commission, a municipally owned utility, has expressed interest in the use of renewable hydrogen for power generation. Initial meetings with Dougherty County officials to propose a non-operational role were held and they are interested in participating. Collaboration with researchers and modelers at JPL was initiated. In addition, close cooperation with other related projects at NREL and JPL is constantly maintained. A special interest among the partners is the identification of other co-roduct options for expanded deployment opportunities. Emissions monitoring will be performed to assess the environmental impact of the hydrogen blend. A social acceptability study will be

performed to assess how the community views the benefits and risks of this new technology.

Future Work

The approach for the next stage is to address the remaining engineering research and development questions related to the conversion of pyrolysis vapors and/or bio-oil to hydrogen, so that a demonstration of the overall concept of biomass to hydrogen can be successful. The use of bio-oils derived from slow pyrolysis of biomass in a reforming operation and the direct coupling of vapors from pyrolysis to steam reforming have not been previously attempted. Process research is required to identify the best operating conditions. Catalyst performance and lifetime will be assessed and data collected on catalyst regeneration. this information will be used in the development of the catalyst regenerator. The other tasks will continue to focus on feedstocks, hydrogen storage options, fuel utilization and partnership development, and are essential to the development of a demonstration of the technology. This will allow commercial evaluations of the concept to be made.

Specific future work and milestones include: gather data for estimating model parameters and run logistical model for Georgia with peanuts as feedstock; quantify importance of transportation costs in biomass processing and identify other biomass feedstocks available in Georgia; perform experiments of liquid-liquid equilibrium on representative compounds found in bio-oils; setup, shakedown and operate continuously reactor at Scientific Carbons site; design hydrogen storage and utilization system for transportation demonstration; cost-effective local bus demonstration on hydrogen utilization; develop a fuel cell based hydrogen utilization effort with the Albany Water, Gas & Light Commission; establish additional non-operational partners in Y2 (2001/2002) & Y3 (2002/2003); and incorporate hydrogen technology in student training and education at Clark Atlanta University.

Conclusions

Biomass as a product of photosynthesis is a renewable resource that can be used for sustainable production of hydrogen. However, direct production of hydrogen from biomass by gasification/water-gas shift technology is unfavorable economically, except for very low cost feedstocks and very large plants. Our approach proposes an alternative strategy with potentially better economics resulting from combined production of hydrogen with valuable co-products. The concept is based on a two-stage process: slow pyrolysis of biomass to generate activated carbon and bio-oil, and catalytic steam reforming of the oil or its fractions to produce hydrogen. The design and utilization of the fluid-bed reformer was completed and shakedown of the reactor is to be completed by Summer 2001. Phase 2 of the project will focus on the long term catalyst testing at Scientific Carbons.

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