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FLUIDIZED BED PYROLYSIS TO GASES CONTAINING OLEFINS

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ABSTRACT

Recent gasification data is presented for a system designed to produce liquid hydrocarbon fuel from various biomass feedstocks. The factors under investigation were feedstock type, fluidizing gas type, residence time, temperature and catalyst usage. The response was gas phase composition. A fluidized bed system was utilized with a separate regenerator-combustor. An olefin content as high as 39 mole % was achieved. Hydrogen/carbon monoxide ratios were easily manipulated via steam addition over a broad range with an autocatalytic effect apparent for most feedstocks.

INTRODUCTION

A process to convert biomass materials to quality liquid hydrocarbon fuels has been under development at Arizona State University since 1975. An indirect liquefaction approach is utilized, i.e., gasification followed by catalytic liquid fuels synthesis. The advantage of indirect liquefaction (vs. direct) is minimization of oxygenated compounds in the liquid hydrocarbon fuel product. The use of catalysts in the liquid fuels synthesis results in very mild processing conditions, i.e., low pressures, temperatures and residence times.

The potential products from the system are indicated on Figure 1. The medium Btu pyrolysis gas (500 + Btu/SCF) conceivably could be used as a fuel gas. The project objective however has always been to tailor the gas composition with respect to carbon monoxide, hydrogen and olefins for use as a synthesis gas for the liquid fuels system. The first reactor in the liquid fuels system contains a Fischer-Tropsch type catalyst. The condensible hydrocarbon phase is a narrow range light paraffinic fuel (C_5 - C_{17}) which can be readily tailored to match diesel, kerosene or jet fuels. If a high octane gasoline is desired, a conventional catalytic reforming step is used to achieve the desired effect.

DISCLAIMER

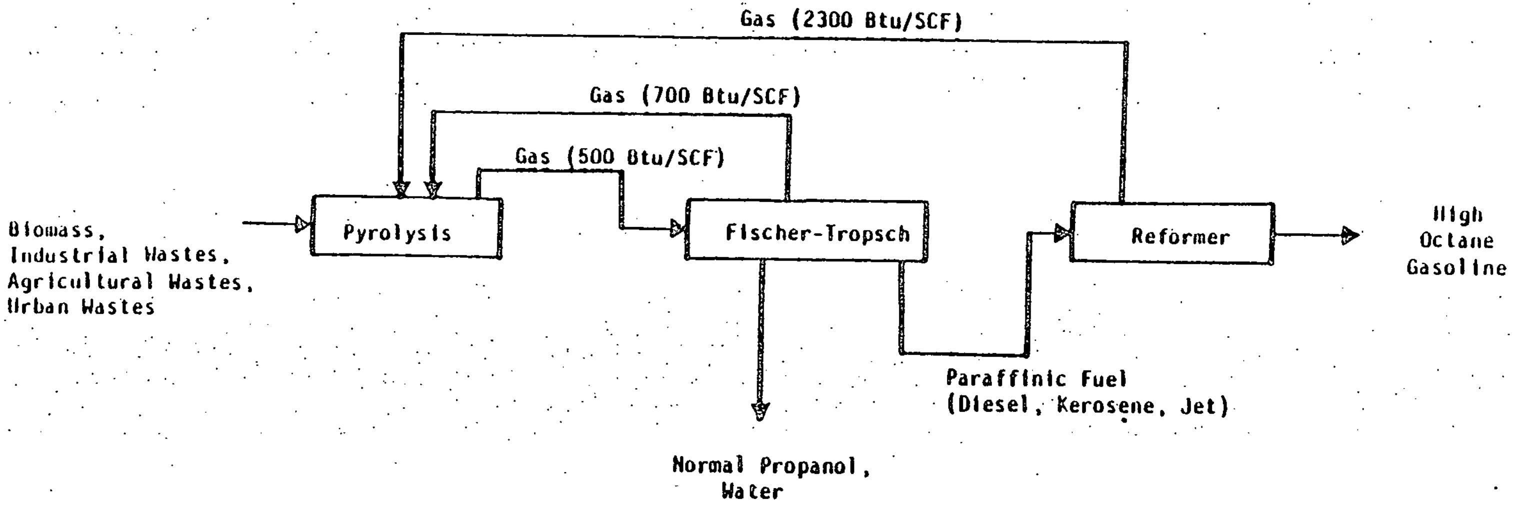

Figure 1.

<u>Basic Chemical Conversion Scheme</u>

A secondary condensible phase from the Fischer-Tropsch step is essentially a binary of normal-propanol and water. The off gases from the liquid fuels reactors are heavy in the low molecular weight paraffins (C_1 - C_5) and thus are of high heating value. It is anticipated that these would be recycled back to the gasification system.

The research scale process has a capacity of about 25 lbs/hr of feedstock. A flow diagram is shown in Figure 2. A fluidized bed with separate regenerator is employed for the pyrolysis step. The heat transfer medium can either be catalytic or inert. The system (both functionally and operationally) is a direct analogy to a catalytic cracker in a petroleum refinery which has been successfully employed since the 1940's. A fluidized bed is also used for the Fischer-Tropsch step (to control the temperature). The reformer is a fixed catalytic bed. Equipment and procedure development have accompanied factor studies for the chemical reactor systems. Previous experimental results for the process have been reported in several publications [1-5]. These include a 2^2 factorial design (temperature, feed rate) for pyrolysis, a 2^3 central composite design (CO, H_2, C_2H_4 feed composition) and temperature, pressure, catalyst loading studies for the Fischer-Tropsch system and a 2^3 central composite design (temperature, pressure, feedrate) for the catalytic reformer. In each case, the responses were the product yields and composition. Additional physical properties were reported (octane number, cetane number, heating values, specific gravity, etc.). In this paper the following additional studies will be presented:

1) gasification data for alternative feedstocks,
2) temperature effects on gasification performance,
3) steam and residence time effects on gasification performance, and
4) water gas shift catalyst effects.

FEEDSTOCK STUDY

A large number of feedstocks were investigated through the gasification step. (Table 1). The industrial wastes refer to by-products of industrial processes. The forest residues tested are all cut by the U. S. Forest Service in the southwest United States for water conservation purposes and burned in the field. Environmental pressures will preclude burning in the future. Eco-Fuel II is a preprocessed municipal refuse. Almond prunings are cut and burned in the almond orchards and thus represent an environmental problem. Russian thistle (tumbleweeds), raw guayule, water hyacinth and peat represent materials that might be harvested deliberately for energy production purposes. Some of the feedstocks were tested at the initiative of the Principal Investigator while others were at the request of the industrial concerns, government agencies and other University laboratories. Elemental and ash analysis for some of the feedstocks are listed in Tables 2 and 3. As indicated, the carbon, hydrogen, oxygen and nitrogen compositions are similar for the biomass materials. The sulfur content is very low except for preprocessed municipal refuse (Eco-Fuel II). The ash content does vary significantly for the materials, ranging from negligable for the synthetic polymers to over 15% for a few materials (e.g., Eco-Fuel II, Russian thistle, water hyacinth).

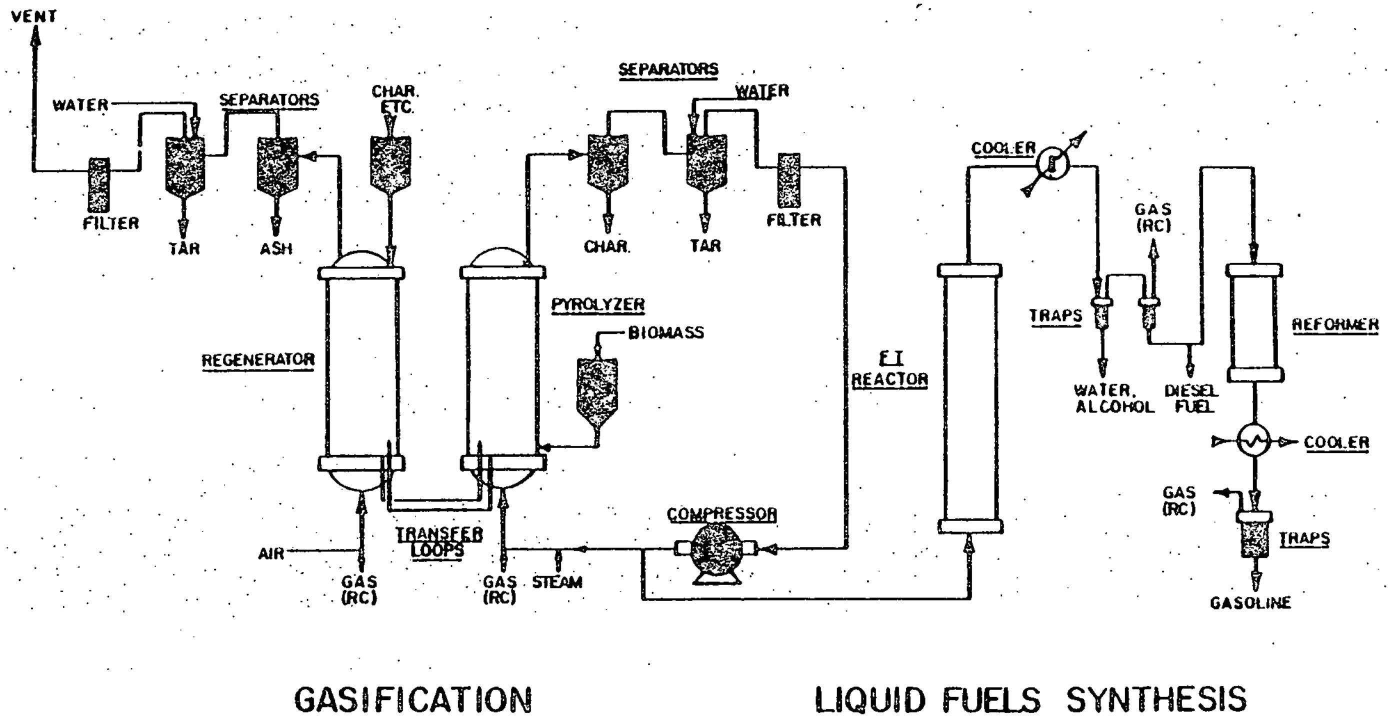

Figure 2.

CONVERSION SYSTEM SCHEMATIC

Table 1

FEEDSTOCKS

Industrial Wastes

- Sawdust
- firbark
- guayule bagasse
- guayule cork
- jojoba meal
- almond hulls
- almond shells
- paper chips
- polyethylene
- polypropylene

Forest Residues

- creosote bush
- sugar sumac
- Arizona cypress
- pringle manzanita
- Wright silktassel
- pointleaf manzanita
- shrub live oak
- hairy mountain mahogany
- Utah juniper
- pinion pine
- mesquite

Urban Wastes

- Eco-Fuel II

Agricultural Wastes

- almond prunings

Energy Crops

- Russian thistle
- raw guayule
- water hyacinth
- peat

Table 2

FEEDSTOCK ANALYSIS

(WT %)

Sample Marking	% Nitrogen	% Sulfur	% Ash	% Loss On Ignition
Guayule - Cork	0.91	0.34	3.53	96.47
Guayule - Bagasse	0.66	0.11	3.27	96.73
Guayule - Raw	0.81	0.18	5.14	94.86
Jojoba Meal	3.94	0.36	3.04	96.96
Water Hyacinth	1.87	0.53	18.97	81.03
Almond - Hulls	0.88	0.08	5.91	94.09
Almond - Shells	0.68	0.03	8.75	91.25
Almond - Cured Prunings	1.01	0.21	25.44	75.46
Eco II - Brockton	0.50	1.44	24.41	75.59
Sawdust	0.28	0.12	7.03	92.97
Paper Chips	0.13	0.08	0.58	99.42

Russian Thistle	1.33	0.19	15.45	84.55
Peat	0.97	0.15	7.63	92.37
Polyethylene	0.09	0.17	0.04	99.96
Polypropylene	0.13	0.03	0.03	99.97

Table 3

FEEDSTOCK ANALYSIS
(WT%)

	Eco Fuel II (Brockton)	Paper Chips	Guayule Bagasse
C	38.0	41.7	40.2
H	4.9	5.7	4.7
O	31.4	52.1	48.4

Table 4

PYROLYSIS OPERATING CONDITIONS

Temperature, °F	1200-1700
Pressure, psig	0-1
Residence Time, Sec	3-6
Feed Rate, lbs/hr	2-15
Heat Transfer Media	sand

Gasification operating conditions for the feedstock survey runs are listed in Table 4. The runs were performed over a period of several months and some equipment modifications were implemented (e.g., feeder modification). Pyrolysis gas composition data is shown in Tables 5-7. Gas phase yield measurements varied from 50-97% but were subject to some experimental error due to lack of a continuous feedback measurement from the solids feeder and occasional coating of the venturi gas flow meter.

The operating conditions for the gasification data should not be considered optimal but are representative of the state-of-the-art of the system at the time the runs were performed. Thus for a given feedstock, improvements in performance are anticipated.

All the cellulosic feedstocks yield a gas with a heating value of about 500 Btu/SCF. The gas from the synthetic polymers has a much higher heating value due to the absence of oxygenated compounds. The gas composition results are masked somewhat by the variation in operating conditions for the different runs. However, several conclusions can be drawn:

1) The more cellulosic type feedstocks yield the lowest total olefin content (generally in the 5-15 mole % range).
2) Materials containing hydrocarbon materials (e.g., oils, latex, synthetic polymers) result in total olefin yields in the 10-25 mole % range.
3) Pure synthetic carbon chain polymers result in total olefin yields of over 30 mole %.
4) Hydrogen/carbon monoxide mole ratios of 0.25 to 0.95 are encountered for dry feedstocks without steam addition (excluding the synthetic polymers).
5) H_2S was not detected for any feedstock. This includes high sulfur materials such as Eco-Fuel II. This is of significance with regard to potential effects on catalyst activity downstream.

Previous studies [1-5] on the system have indicated that an optimal pyrolysis gas composition for maximizing liquid hydrocarbon fuel yields is 20 mole % + olefins and a H_2/CO ratio of 1-1.5. Selected feedstocks are capable of producing the desired amounts of olefins (e.g., guayule cork). Without steam addition, all the materials (except the synthetic polymers) result in a suboptimal H_2/CO mole ratio.

TEMPERATURE STUDY

Gas phase composition results for paper chip feedstock are shown in Figure 3. Only the major components are included in the analysis (H_2, CO, C_2H_4, C_2H_6, CH_4, CO_2). Recycle pyrolysis gas was used for fluidization. The feedstock was dry and steam was not fed to the system. However, the recycle gas is saturated with water after passing through the wet scrubbing system. The results shown in Figure 3 indicate an apparent water gas shift effect with increasing temperature with a corresponding decline in paraffin and olefin production. When considering that gas phase yields increase with increasing

Table 5.

PYROLYSIS GAS COMPOSITION (mole %)[1]

Feedstock:	Almond Hulls	Almond Shells	Almond Prunings	Poly-ethylene	Polypro-pylene	Paper Chips	Peat[2]
H_2	28.08	26.03	25.70	14.19	13.57	14.77	45.05
O_2	0.00	0.00	0.16	0.00	0.00	0.23	0.00
CO	35.44	38.06	42.68	0.96	0.69	58.86	18.48
CO_2	13.92	12.15	5.97	0.23	0.00	3.27	16.29
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	14.96	17.21	14.88	43.56	42.43	14.76	10.69
C_2H_2	0.05	0.06	0.17	0.61	1.18	0.10	0.12
C_2H_4	4.01	3.09	5.68	19.29	13.34	3.70	4.15
C_2H_6	1.29	1.72	1.05	6.78	6.13	2.26	1.88
C_3 olefins	1.23	0.54	0.21	5.30	9.77	1.21	1.21
C_3H_8	0.03	0.06	0.00	0.00	0.00	0.08	0.09
C_4 olefins	0.12	0.10	0.08	0.59	3.64	0.18	0.19
C_4H_{10}	0.00	0.00	0.01	0.02	0.06	0.00	0.01
C_5H_{12}	0.01	0.01	0.00	0.00	0.00	0.00	0.02
C_5 + olefins	0.86	0.97	3.41	7.49	9.20	0.57	1.83
total unsaturated	6.27	4.76	9.55	33.28	37.13	5.76	7.38
H_2/CO ratio	0.79	0.68	0.60	14.78	19.67	0.25	2.44

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[1] - water, nitrogen free basis

[2] - Steam fluidization with recycle pyrolysis gas to sparges (other runs with total recycle gas)

Table 6.

PYROLYSIS GAS COMPOSITION (mole %)[1]

Feedstock:	Fir Bark	Sugar Sumac	Raw Guayule	Guayule Bagasse	Guayule Cork	Russian Thistle	Water Hyacinth	Sawdust	Jojoba Meal	Eco-Fuel II
H_2	16.58	28.89	17.28	25.02	20.57	26.37	23.00	15.13	11.96	15.74
O_2	0.10	0.00	0.00	0.07	0.17	0.00	0.00	0.42	0.41	0.05
CO	53.42	31.88	34.98	39.61	22.14	36.08	42.43	55.57	37.56	50.40
CO_2	2.99	10.57	8.51	6.11	3.77	14.62	13.94	5.31	10.32	3.20
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	18.07	15.16	26.17	15.36	26.03	16.23	14.34	16.37	23.21	15.03
C_2H_2	0.05	0.01	0.04	0.21	0.05	---	0.00	0.10	0.00	0.00
C_2H_4	5.71	5.75	5.57	7.14	14.80	3.21	3.52	2.63	9.15	6.04
C_2H_6	1.60	2.85	2.31	0.63	4.79	1.69	1.62	2.36	3.44	3.60
C_3 olefins	0.37	1.81	1.50	0.00	3.04	0.61	0.57	1.13	2.01	2.03
C_3H_8	0.01	0.41	0.05	0.13	0.16	0.02	0.02	0.09	0.03	0.10
C_4 olefins	0.18	0.65	0.56	0.06	0.83	0.14	0.13	0.20	0.45	0.51
C_4H_{10}	0.02	0.00	0.01	0.00	0.08	0.01	0.00	0.01	0.01	0.11
C_5H_{12}	0.00	0.00	0.04	0.00	0.00	0.01	0.08	0.00	0.80	0.00
C_5 + olefins	0.91	2.20	2.97	5.64	3.58	1.02	0.35	0.67	1.78	3.13
total unsaturated	7.22	10.42	10.64	13.05	22.30	4.98	4.57	4.73	13.39	11.71
H_2/CO ratio	0.31	0.91	0.49	0.63	0.93	0.73	0.54	0.27	0.32	0.31

1 - water, nitrogen free basis

Table 7.

PYROLYSIS GAS COMPOSITION (mole %)[1]

Feedstock:	Arizona Cypress	Pringle Manzanita	Creosote Bush	Pinion Pine	Wright Silktassel	Utah Juniper	Pointleaf Manzanita	Shrub Live Oak	Hairy Mountain Mahogany	Mesquite
H_2	26.64	24.99	25.99	25.82	25.64	28.83	24.46	27.99	27.61	33.01
O_2	0.07	0.04	0.03	0.44	0.04	0.05	0.34	0.07	0.04	0.06
CO	38.40	40.68	39.43	41.78	38.69	39.54	35.50	41.28	37.84	44.35
CO_2	7.04	6.76	7.70	4.39	5.43	6.41	10.58	4.53	4.76	5.10
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	15.82	15.10	15.61	15.68	16.56	16.20	14.08	16.86	15.32	12.11
C_2H_2	0.01	0.11	0.02	0.14	0.17	0.11	0.15	0.11	0.30	0.03
C_2H_4	6.40	6.29	6.48	6.33	7.30	6.56	5.64	5.56	10.26	2.61
C_2H_6	1.65	1.29	0.93	1.87	1.68	1.60	2.00	1.12	1.53	0.18
C_3 olefins	0.65	0.44	0.45	0.28	0.53	0.43	1.21	0.15	0.67	0.00
C_3H_8	0.02	0.01	0.05	0.01	0.05	0.02	0.08	0.01	0.04	0.17
C_4 olefins	0.21	0.10	0.18	0.08	0.15	0.12	0.29	0.09	0.16	0.01
C_4H_{10}	0.03	0.02	0.02	0.01	0.03	0.04	0.12	0.01	0.02	0.00
C_5H_{12}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_5 + olefins	3.07	4.17	3.11	3.17	3.74	0.11	5.56	2.22	1.44	2.36
total unsaturated	10.34	11.11	10.24	10.00	11.89	7.33	12.85	8.13	12.83	5.01
H_2/CO ratio	0.69	0.61	0.66	0.62	0.66	0.73	0.69	0.68	0.73	0.74

[1] - water, nitrogen free basis

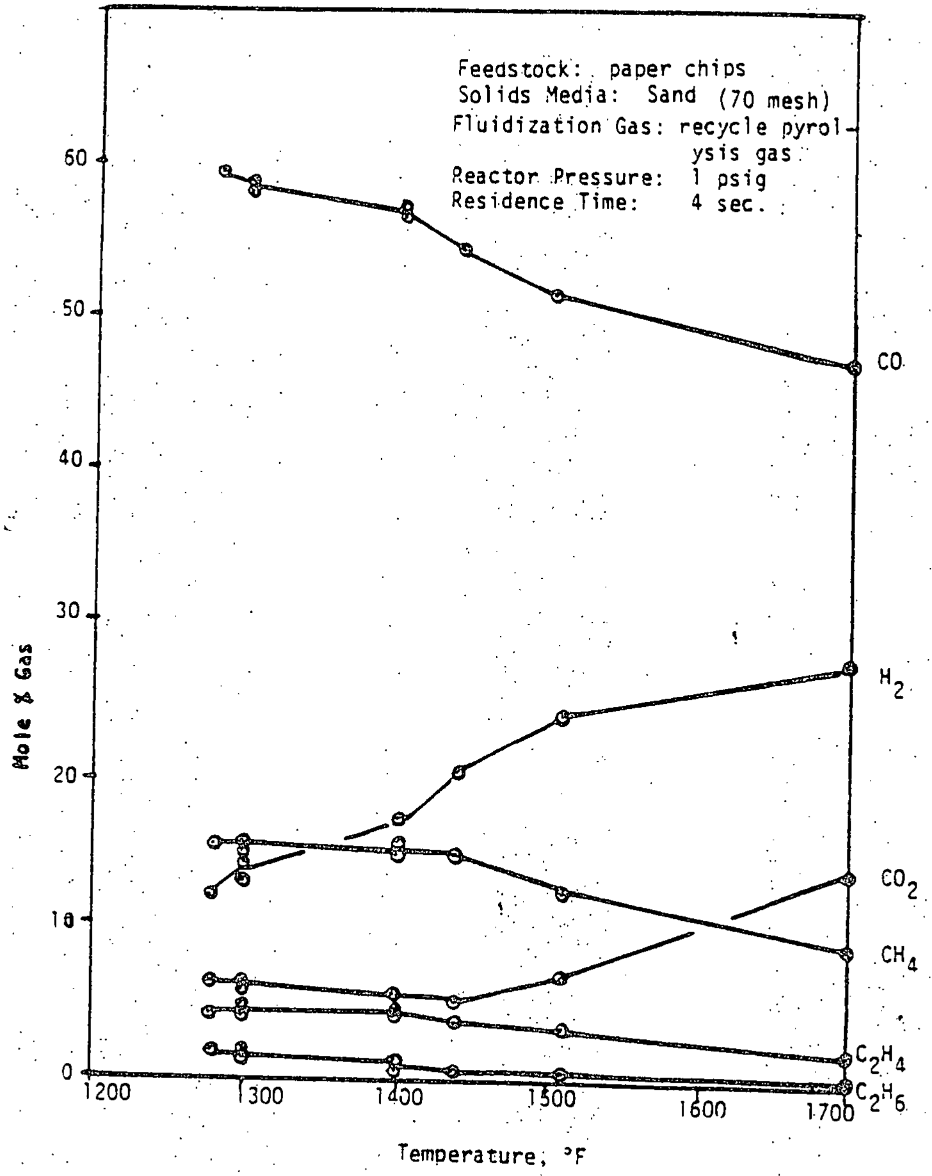

Figure 3.

PYROLYSIS GAS COMPOSITION vs. TEMPERATURE

temperature and that an optimal balance of carbon monoxide, hydrogen and olefin production is desired, it is apparent that temperature alone is insufficient as a control variable in the gasification system.

FLUIDIZING GAS, RESIDENCE TIME, CATALYST STUDY

It is difficult to isolate the effects of fluidizing gas type and composition and residence time in a fluidized bed system. Thus for a given reactor size, lower residence times are achieved by increasing the gas throughput. This is constrained by proper particle size to prevent excessive solids carryover. Experimentation in this area consisted of steam addition to the system with fixed reactor dimensions and particle size. Results for various feedstocks are shown in Tables 8-10. The steam was superheated to approximately 600°F via a coil in the gasification system combustor. With this system, the reactor temperature was lowered with a significant amount of steam addition to the pyrolyzer. For fir bark and guayule cork feedstock (Tables 8, 9), an increase in unsaturated compounds and H_2/CO ratio were observed with steam addition. An autocatalytic water gas shift reaction effect is apparent in each case. This could be due to the presence of mixed metal oxides in the ash content of the biomass (similar to commercial water gas shift catalyst composition). Eco-Fuel II feedstock did not exhibit as significant a water gas shift effect (Table 10). However, the H_2/CO ratio was increased by a factor of 7 when a section of the reactor overhead line was packed with a commercial water gas shift catalyst. In general, it appears that the H_2/CO ratio can be manipulated with steam addition for virtually any feedstock candidate. If an autocatalytic effect is not present, a simple fixed bed shift catalyst section will achieve the desired result. Olefin production appears more complicated. The most dramatic effect occurred with guayule cork feedstock with an increase from 22 to 39% with steam addition. This however corresponded to a substantial reduction in residence time (8 to 1 seconds) and may also be feedstock dependent. Current research is aimed at lowering the residence time to less than one second via a combination of steam addition and recycle off gas from the liquefaction system. The liquefaction off gas normally would be depleted of hydrogen and olefins and thus use of this gas would avoid an effective increase in residence time with respect to these components as is the case when recycling pyrolysis gas.

SUMMARY, CONCLUSIONS, CONTINUING RESEARCH

The particular experiments emphasized in this paper lead to the following conclusions:

1) A wide variety of feedstocks can be processed through the gasification system to a gas with a heating value of 500 + Btu/SCF.
2) Some feedstocks are more attractive than others with regard to producing a high olefin content. This appears to be related to hydrocarbon content of the material.
3) The H_2/CO ratio can be manipulated over a wide range in the gasification system with steam addition. Some feedstocks require the aid of a water gas shift catalyst while others appear to exhibit

Table 8.

STEAM EFFECT - FIR BARK FEEDSTOCK

	No Steam	Partial Steam
Operating Conditions:		
temperature, °F	1400	1250
pressure, psig	0.9	0.9
residence time, sec.	4	3.2
feed rate, lbs/hr	5	5
heat transfer media	sand	sand
fluidizing gas	pyrolysis gas	pyrolysis gas + steam
Pyrolysis Gas Composition (mole %)[1]:		
H_2	16.58	29.24
O_2	0.10	0.14
CO	53.42	44.41
CO_2	2.99	3.33
H_2S	0.00	0.00
CH_4	18.07	10.60
C_2H_2	0.05	0.03
C_2H_4	5.71	7.30
C_2H_6	1.60	0.54
C_3 olefins	0.37	1.93
C_3H_8	0.01	0.06
C_4 olefins	0.18	0.46
C_4H_{10}	0.00	0.00
C_5H_{12}	0.00	0.00
C_5 + olefins	0.91	1.89
total unsaturated	7.13	11.58
H_2/CO ratio	0.31	0.66

1 - water, nitrogen free basis

Table 9.

STEAM-RESIDENCE TIME-RECYCLE EFFECTS
(Guayule Cork Feedstock)

	No Steam	Steam
Operating Conditions:		
temperature, °F	1300	1200
pressure, psig	0.9	0.9
residence time, sec	8	1
feed rate, lbs/hr.	5	5
heat transfer media	70 mesh sand	70 mesh sand
fluidizing gas	recycle pyrolysis gas	recycle pyrolysis gas + steam
Pyrolysis Gas Composition (mole %)[1]:		
H_2	20.57	24.51
O_2	0.17	0.47
CO	22.14	10.87
CO_2	3.77	10.76
H_2S	0.00	0.00
CH_4	26.03	10.95
C_2H_2	0.05	0.04
C_2H_4	14.80	16.67
C_2H_6	4.79	3.24
C_3 olefins	3.04	6.49
C_3H_8	0.16	0.25
C_4 olefins	0.83	2.65
C_4H_{10}	0.08	0.21
C_5H_{12}	0.00	0.00
C_5 + olefins	3.58	12.88
total unsaturated	22.30	38.73
H_2/CO ratio	0.93	2.25

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[1] - water, nitrogen free basis

Table 10.

STEAM EFFECT - ECO-FUEL II FEEDSTOCK

	No Steam	Steam	Steam + Water-Gas Shift Catalyst
Operating Conditions:			
temperature, °F	1250	1180	1260
pressure, psig	0.9	0.9	1.5
residence time, sec.	4	5	5
feed rate, lbs/hr	4	4	8
heat transfer media	sand	sand	sand
fluidizing gas	pyrolysis	pyrolysis gas + steam	pyrolysis gas + steam
Pyrolysis Gas Composition (mole %)[1]:			
H_2	16.81	23.62	42.59
O_2	0.09	0.08	0.00
CO	50.62	45.24	17.18
CO_2	2.30	3.74	12.52
H_2S	0.00	0.00	0.00
CH_4	15.92	11.34	16.45
C_2H_2	0.02	0.05	0.11
C_2H_4	7.14	7.90	5.03
C_2H_6	3.43	2.26	3.67
C_3 olefins	1.72	2.51	1.03
C_3H_8	0.11	0.17	0.03
C_4 olefins	0.25	0.78	0.30
C_4H_{10}	0.04	0.06	0.02
C_5H_{12}	0.00	0.00	0.02
C_5 + olefins	1.56	2.23	1.05
total unsaturated	10.67	13.42	7.52
H_2/CO ratio	0.33	0.52	2.48

1 - water, nitrogen free basis

an auto-catalytic effect to achieve the conversion.

4) H_2S content (beyond the gasification system wet scrubber) is negligible for the feedstocks surveyed.

5) The water gas shift reaction appears to be enhanced with an increase in pyrolysis reactor temperature over the range of 1300 - 1700°F.

Continuing research includes integrated system performance assessment, alternative feedstock characterization and factor studies for gasification (e.g., catalyst usage, alternate heat transfer media, steam usage, recycle effects, residence time study) and liquefaction (e.g., improved catalysts, catalyst activity characterization). An additional task in progress includes the characterization of various feedstocks by compound types and corresponding correlation with reactor system performance.

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