Experimental Analysis of Steam and CO_2 Gasification of Biomass Fuels

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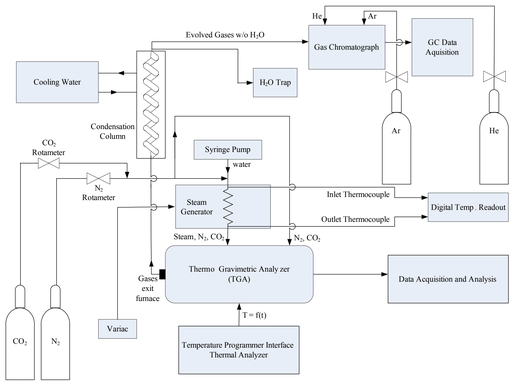
Introduction

- This study examines the influence of gasification medium and heating rate on thermo-chemical conversion of biomass fuels. Two thermal regimes, whose transition occurred about 400°C, were observed for both the mass decay and gas evolution profiles of all feedstocks studied.
- While steam gasification offers enhanced H_2 production, when CO_2 is used as the gasification medium a more complete conversion to volatiles can be achieved. CO_2 injection was found to enhance the CO evolution and depress the H_2 production during gasification. This offers the opportunity to tune the syngas ratio to a more suitable value for use in a particular application.
- Though the gasification decomposition behavior for all biomass feedstocks was intermediate between those of the structural components lignin and cellulose, the pyrolysis behavior of the herbaceous feedstocks indicated the presence of a catalytic effect causing the pyrolytic degradation to occur significantly earlier.
- By adjusting the level of CO_2 in the gasification medium as well as the heating rate of the TGA furnace, the relative amounts of the lignocellulosic components that can survive thermal degradation can be controlled. While the cellulosic component can be processed at low pyrolysis temperatures, the thermally resistant lignin can survive and remain available for subsequent treatment.
- CO_2 was found to more easily access the char structure and enable the thermally resistant lignin to undergo a more thorough conversion to volatiles with less residual char and corrosive ash for post-processing.

Results



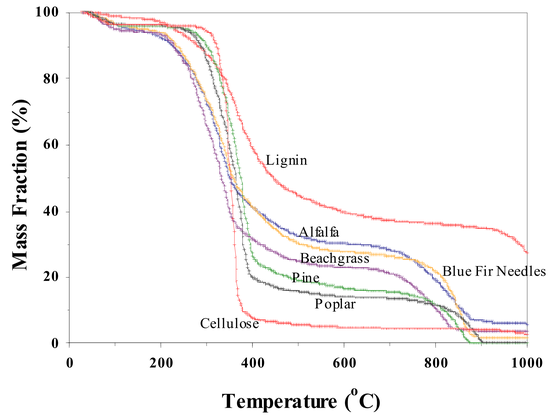
Schematic of experimental apparatus

Biomass Fuel	Classification	HHV (calories/gram)	Cellulose	Hemicellulose	Lignin
Spruce	Softwood	4719	48	21	28
White Pine	Softwood	4781	42	21	26
Douglas Fir	Softwood	4769	41	24	28
Poplar	Hardwood	4699	41	21	24
Sugar Maple	Hardwood	4725	39	30	23
Oak	Hardwood	4782	40	25	26
Alfalfa	Grass	4338	30	14	14
Cordgrass	Grass	4448	43	33	16
Beachgrass	Grass	4329	45	31	12
Wheat Straw	Grass	4402	38	29	14
Maple Bark	Bark	4316	18	33	19
Bl. Fir Needle	Needles	4278	38	24	31
Pine Needle	Needles	4350	43	22	38
Gr. Olive Pit	Shell/Pit	5165	-	-	-
Pecan Shell	Shell/Pit	4371	38	23	29
Almond Shell	Shell/Pit	4553	-	-	-
Walnut Shell	Shell/Pit	4823	-	-	-
Peanut Shell	Shell/Pit	4732	36	19	30
Rice Hull	Hull/Husk	4575	6	-	25

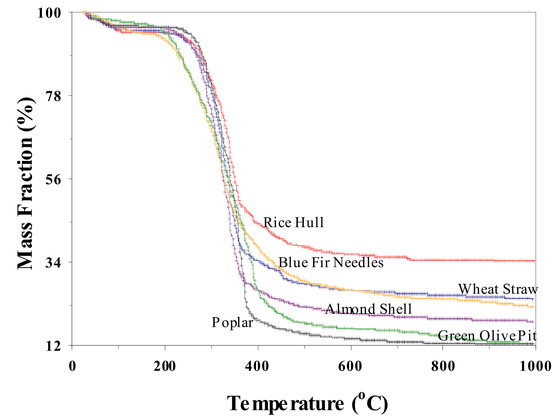
Characterization of Biomass Feedstocks

Results

More thorough processing of biomass feedstocks to volatiles is possible through the use of a CO_2 gasification medium.



Mass decomposition curve for CO_2 gasification (10°C/min, 100% CO_2)



Mass decomposition curve for steam gasification (10°C/min, 0% CO_2)

With as little as 30% CO_2 injection into the gasification environment, a small mineral residue results rather than a large volume of black char.

Enhanced Char Burnout With CO_2 Injection

0% CO_2 Douglas Fir steam gasification

30% CO_2 Douglas Fir steam gasification

0% CO_2 Walnut Shells steam gasification

30% CO_2 Walnut Shells steam gasification

Results

The thermally resistant lignin results in a hard glassy surface that resists slow thermo-chemical conversion using a H_2O/N_2 medium, in contrast to the highly porous network that develops in a pure CO_2 gasification environment and which accounts for the enhanced conversion at the slow 1°C/min heating rate.

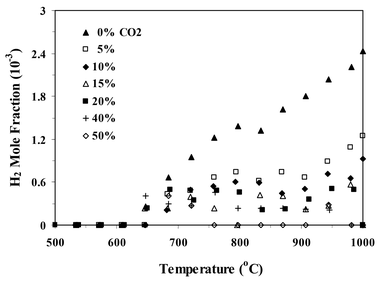
Char Pore Development- Enhanced Char Burnout With CO_2

Lignin, 0% CO_2, 1°C/min, 22-860°C H_2O/N_2

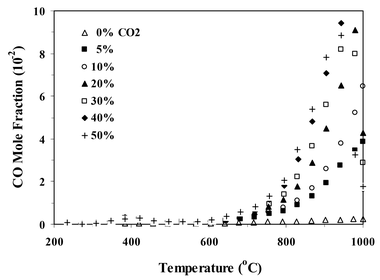
Lignin, 100% CO_2, 1°C/min, 22-860°C

Lignin, 100% CO_2, 1°C/min, 22-930°C

CO_2 injection was observed to enhance CO and depress H_2 and CH_4 evolution for all feedstocks examined- woods, grasses, agricultural and forestry residues.

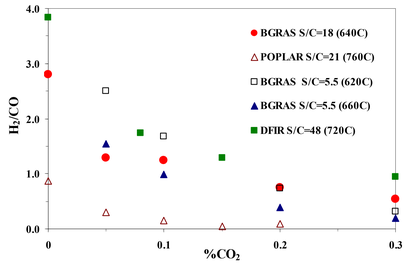


H_2 Evolution Depression from poplar using CO_2



CO Evolution Enhancement from beachgrass using CO_2

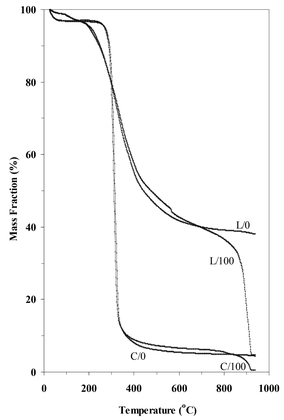
The ability of CO_2 to depress the levels of H_2 and enhance the levels of CO produced during thermal treatment enables greater control of the H_2/CO syngas ratio resulting in a more suitable product gas for applications such as fuel cells, Fischer-Tropsch synthesis or specialty chemicals production.



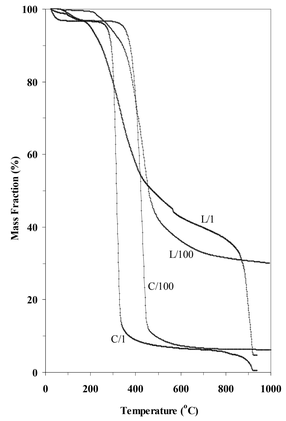
H_2/CO ratio tuning through variation of CO_2 injection level

Results

Use of CO_2 (100%) rather than steam (0%) during thermal treatment results in more complete processing at high gasification temperatures while the use of a slow heating rate (1°C/min) results in the ability to retain a greater portion of the lignin component while removing most of the cellulosic fraction-greater control in structural component separation. Thermal treatment at lower T is possible since at slower heating rates mass decomposition profiles shift to lower T.



Mass decomposition curve for Lignin and Cellulose, 1°C/min, comparing steam (0%) and CO_2 (100%) gasification



Mass decomposition curve comparing Lignin and Cellulose, 100% CO_2, 1°C/min and 100°C/min

Conclusion

- Use of CO_2 results in more complete thermo-chemical processing of lignocellulosics
- CO_2 creates a more porous char structure and is more able to access the porous network
- Biomass gasification rates were found to be intermediate between that of easily pyrolyzed polysaccharide cellulose and thermally resistant aromatic lignin
- Lignin decomposition began slightly earlier than cellulose though it extended over a much longer T interval (225-800°C) as compared to cellulose (275-425°C)
- Using CO_2 rather than H_2O/N_2 and a very slow heating rate (~1°C/min), cellulosic component can undergo conversion at low pyrolytic Ts retaining a relatively greater fraction of lignin component available for subsequent processing
- Since CO_2 can depress H_2 and enhance CO evolution during gasification, it offers greater control in the thermal treatment process by enabling the "tuning" of the H_2/CO syngas ratio to meet the needs of a particular application
- A least squares fit on the rate of mass loss fraction gave a global decomposition during pyrolysis of third order for lignin in CO_2 and H_2O/N_2, first order for cellulose and either first or second order for the various biomass samples. Gasification showed a best overall correlation with first order
- CO_2 pyrolysis (110-450°C) global activation energies for lignin, cellulose and biomass were 22-49, 202-230 and 28-72 kJ/mole. CO_2 gasification (500-700°C) energies for lignin and biomass were 12-38 and 9-57 kJ/mole. In H_2O/N_2 the lignin values were 38-58 during pyrolysis and 3-23 kJ/mole during gasification