Research and Development

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Project Summary

A Study of the Steam Gasification of Organic Wastes

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Chemical kinetic data describing the pyrolysis/gasification characteristics of organic waste (biomass) materials is needed for the design of improved conversion reactors. Unfortunately, little data is available in the literature on the pyrolysis kinetics of waste materials, and essentially no data has been published on the rates and products of the secondary, gas phase reactions. The objective of this research was to determine the effects of various reactor conditions (residence time, temperature, and heating rate) on the rates of the primary pyrolysis reactions, and the rates and products of the secondary gas phase reactions.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In an age of diminishing fossil fuel reserves, as reflected in rapidly escalating prices for fluid fuels, local shortages of gasoline and fuel oil, and large imbalances in international trade, attention has recently focused on fluid fuel production from renewable biomass* resources. Pyrolysis is one attractive method for converting biomass to more useful fuel

forms. Unfortunately, the product slate of most pyrolysis processes includes significant quantities of relatively valueless tars, oils, pitches, liquors and some water soluble organic compounds. These valueless products of conversion processes adversely affect process economics because they reduce conversion efficiencies, and require more complicated equipment for their handling and ultimate disposal.

The primary goal of this research was to experimentally determine the conditions required for the conversion of these valueless products into a hydrocarbonrich synthesis gas. To accomplish this goal, the research effort focused primarily on an elucidation of the chemistry of waste pyrolysis/gasification in steam. Since kinetic information is essential for the development of improved gasification systems, all experiments were designed and conducted to provide carefully characterized rate data. When possible, this data was interpreted using Arrhenius kinetics, and mathematical models were developed to fit the experimental data. Although these models were not intended to be of fundamental import, they are expected to be of great use to chemical engineers in designing advanced gasification systems.

Summary and Conclusions

The gasification characteristics of biomass differ considerably from those of coal, lignite, peat and other fossil fuels. Research described in this report has shown biomass gasification to be a threestep process:

^{*}Because their thermochemical properties are similar, the words "biomass" and "organic wastes" are used interchangeably throughout this report.

- Pyrolysis. At modest temperatures (300 ° to 500°C) biomass materials lose between 70% to 90% of their weight by pyrolysis, forming gaseous volatile matter and solid char. Biomass materials contain much more volatile matter than does coal, and biomass loses weight more rapidly than coal by pyrolysis.
- Cracking/Reforming of the Volatile Matter. At somewhat higher temperatures (600°C or more), the volatile matter evolved by the pyrolysis reactions (step 1 above) reacts in various ways to form a hydrocarbon rich synthesis gas. These reactions occur very rapidly (seconds or less) and can be manipulated to favor the formation of various hydrocarbons (such as ethylene).
- Char Gasification. At even higher temperatures (800°C or more) char gasification occurs by reactions

 $C + H_2O - CO + H_2$ $C + CO_2 - 2CO$ $C + 1/2 O_2 - CO$ $C + O_2 - CO_2$

These reactions can be used to describe coal gasification, but proceed more slowly and under more demanding conditions than those required for steps 1 and 2. Since step 1 produces less than 30% by weight char, these char gasification reactions play a minor role in biomass gasification.

Although each of these three steps play a role in commercial reactors designed for biomass gasification, the ultimate product slate of the reactor is largely determined by the second step of the gasification process. Careful control of reactor conditions (i.e., gas phase residence time and temperature) can favor the production of valuable hydrocarbons (olefins and paraffins) from biomass over a less valuable synthesis gas (CO and H₂), or valueless tars, liquors and oils. The focus of the full report is the determination of those conditions which favor the formation of hydrocarbons from biomass using thermochemical conversion techniques. The conclusion is that surprisingly mild conditions are required to effect the conversion of biomass to hydrocarbons.

Those familiar with petrochemical technologies will recognize similarities between the results given in the report and comparable results for steam cracking naphthas and gas oils to ethylene. In fact, biomass may be a more desirable source of olefins than feedstocks traditionally used by the petrochemical industry. Data

given in the report indicate that from a thermochemical viewpoint, biomass is a much more desirable solid fuel feedstock for the production of fluid fuels and chemicals than are coal, lignite or peat.

During the past two years, over 60% of the Princeton research effort on biomass and waste conversion has focused on elucidating the rates and products of the secondary, gas phase reactions of pyrolytic volatile matter in steam (step 2 described above). Results of our research in this area are described in the full report. This research produced the first detailed study of secondary, gas phase reaction rates and products reported in the literature. The most important conclusion resulting from this aspect of the research is that the secondary, gas phase reactions are dominated by cracking chemistry. At temperatures above 700°C, these cracking reactions reach completion in less than one second. Thus the technologies developed for steam cracking naphthas and gas oils are applicable to biomass conversion, and may prove to be the favored conversion route as conversion technologies develop and mature.

A significant effort was also made to study the effects of increased pressure on the products and rates of the primary and secondary pyrolysis reactions. Numerous difficulties were encountered which substantially impeded our progress; nevertheless some early results are reported here.

The remaining part of Princeton's research effort was divided between kinetic studies of the solid phase pyrolysis reactions (step 1 described above), and some exploratory model compound studies aimed at providing an insight into the gas phase chemistry. Despite the great variety of biomass materials studied, their rates and mechanisms of weight loss by pyrolvsis were reasonably similar from an engineering point of view. Kinetic weight loss models, developed to describe the solid phase pyrolysis reactions, are presently being used in a reactor design effort at Princeton. The model compound studies focused on the gas phase pyrolysis of ethanol, used to simulate the cracking chemistry of cellulose volatiles. Competitive reactions forming ethylene, or Ch4, CO and H2 were studied. Cracking rates were measured, and found to compare favorably with literature values. Future research on model compounds will be aimed at determining those conditions which give rise to maximum production of olefins from biomass by offering an insight into the gas phase cracking chemistrv.

Since the research described in this report indicates that biomass and wastes. may be more desirable than coal, peat, or lignite as gasification feedstocks, the former should be thoroughly investigated as synfuel sources. A more thorough investigation of the thermochemical conversion chemistry of biomass and wastes to useful fluid fuels would be necessary before final economic and environmental judgments can be made. These efforts should include studies of gasification mechanisms, kinetics, and catalysis. More attention should be given to the secondary, gas phase reactions of pyrolytic volatile matter. Reactors, designed specifically to study the gas phase chemistry, should be developed. Without a better insight into the gas phase chemistry, biomass gasification reactor design efforts will continue to produce 19th and early 20th century concepts, rather than the 21st century processes needed to compete with today's sophisticated hydrocarbon processing industry.

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The complete report, entitled "A Study of the Steam Gasification of Organic Wastes," (Order No. PB 84-143 148; Cost: \$13.00, subject to change) will be available only from:

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