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Presented at the
3rd Miami International Conference
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# THERMAL DEGRADATION OF CELLULOSE IN ALKALI

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## ABSTRACT

Biomass in an alkaline aqueous slurry can be liquefied by heat and pressure. We are interested in better understanding the mechanisms of biomass liquefaction to improve the efficiency of converting biomass to useful products, particularly chemicals and synthetic fuels.

To study the chemical mechanisms of this process, we liquefied pure cellulose, the main component of biomass; later we plan to expand our study to include lignin and hemi-cellulose. The 78 cellulose liquefaction products that we have identified by gas chromatography/mass spectrometry include polyols, furans, ketones, hydrocarbons, and aromatic compounds. Polyols may be formed by hydrogenolytic cleavage. Furans and cyclic ketones may be cyclization products of dicarbonyl intermediates formed by aldol condensation of small initial degradation products such as acetone and acrolein. We used several of these small carbonyl compounds as model compounds to test our proposed mechanisms for furans and cyclic ketones and obtained products supporting five of the mechanisms. For the best case of 26 cellulose liquefaction experiments, 34% of the initial mass of the cellulose was converted to acetone-soluble oil with a heat of combustion of 14,000 Btu/lb.

## 1. INTRODUCTION

Aqueous, alkaline, thermal liquefaction of cellulosic materials, available as biomass, can help reduce our dependence on natural crude oil. Liquefaction could supply liquid fuels, chemical feedstocks, and synthetic asphalt. Within the last ten years, H. R. Appell and others at the U.S. Bureau of Mines have extensively studied the conversion of cellulosic wastes to liquid fuels (1, 2). Additional studies on this topic are reviewed in an article by Alvin Weiss (3). The review mentions organic chemicals as a valuable product of one conversion process. Further study, including investigation of chemical mechanisms, is needed to improve conversion process and product use efficiency.

At the Pacific Northwest Laboratory (PNL)[a] we are focusing on liquefaction mechanisms in our ongoing work sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences. I will describe our study of chemical mechanisms and the possibility of using liquefaction products as an energy

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[a] The Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

source. A brief discussion of our study of sewage sludge conversion to synthetic asphalt for the city and county of Honolulu, state of Hawaii, and the U.S. Environmental Protection Agency provides an example of liquefaction products from actual biomass.

## 2. STUDY OF CHEMICAL MECHANISMS

To simplify the general problem of biomass liquefaction, we chose to study conversion of cellulose, the most abundant component of biomass. We reacted a 20% slurry of pure cellulose (Solka-Floc®) in water with at least 0.3N sodium carbonate at 270°C to 400°C in high-pressure autoclaves. This process converted up to 34% by weight of the cellulose into acetone-soluble oil. The other products were char, gas, and water-soluble compounds. Details of the conversion procedure are included in two earlier publications (4, 5).

By analyzing 17 oil samples and one aqueous sample we identified 78 compounds as cellulose conversion products. Our main analytical method was gas chromatography/mass spectrometry (GC/MS). Though many more than 78 compounds were indicated by the gas chromatograms, the complex nature of the samples made complete separation of all compounds impossible. Those products that we identified include polyols, furans, ketones, hydrocarbons, and aromatic compounds.

Three well-known reactions could explain the formation of diols, furans and ketones. These groups of compounds constitute 45% of the 78 identified products. Hydrogenolytic cleavage may lead to the polyols. This reaction has been noted in connection with commercial production of polyols (6). Aldol condensation and the closely related Michael reaction are important in the mechanisms leading to furans and cyclic ketones. Small carbonyl compounds such as acetone and acrolein (propenal) may condense to dicarbonyl intermediates that then cyclize to furans and ketones. Currently we are studying the formation mechanisms of the hydrocarbon and aromatic compounds that constitute 46% of the 78 identified conversion products.

To test our proposed mechanisms, we carried out a series of nine model compound experiments. Since the final cellulose liquefaction products identified do not contain the intact glucose ring (the monomer of cellulose) the glucose units must break down, and the breakdown products then recombine to yield the variety of products observed. The small carbonyl compounds such as acetone and acrolein that we used as model compounds are initial degradation products of cellulose. Based on our proposed mechanisms, the nine combinations of intermediates should yield 22 expected products. After we reacted the model compounds under the same conditions that we reacted cellulose, we found eight of the products that we had expected. Seven of the products are common to both cellulose and model compound experiments, supporting five of our predicted mechanisms. Table 1 summarizes the model compound experiments. The 22 expected products are listed beside the appropriate model compounds. The two right-hand columns indicate which of the products we identified in the cellulose products and in the model compound products. The compounds involved in the five supported mechanisms are underlined.

Taking one specific case as an example, we predicted that 2,4-dimethylcyclopentanone could be formed by aldol condensation of propanal and methylacrolein (2-methylpropenal) followed by cyclization. Supporting this

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TABLE 1. Products Expected From Model Compound Experiments Based on our Proposed Mechanisms

|  |  | Confidence Level of Identification* |  |
|---|---|---|---|
| Model Compounds | Expected Products | Cellulose Products | Model Cmpds. |
| Acetone + acetaldehyde | 3-methyl-1-butanol | T |  |
|  | 4-methyl-3-penten-2-one (mesityl oxide) | T | P |
|  | 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol) | T | P |
| Butanal + acetoin | 3-octa-1,4-dienone | T |  |
| Acetaldehyde + acrolein | cyclopentanol | P |  |
|  | cyclopentanone | H |  |
|  | 3-pentenal |  |  |
|  | 1,3-cyclopentadiol |  |  |
|  | cyclopentadiene |  |  |
| Acetone + acrolein | cyclohexanone | H | H |
|  | phenol | H | H |
|  | 2-cyclohexenone |  | H |
|  | cyclohexanol | P |  |
|  | 2-methylcyclopentanone | T |  |
|  | 2-methylcyclopentanol |  |  |
|  | 1-methylcyclopentene |  |  |
| Acetone | 4-methyl-3-penten-2-one | T | H |
|  | 4-hydroxy-4-methyl-2-pentanone | T | H |
|  | 3-methylcyclopentanone | P |  |
| propanal + acetoin | 2,5-dimethyl-2-cyclopentenone | H | P |
|  | dimethylcyclopentadiene |  |  |
| Butanal + acrolein | 2-ethylcyclopentanone | H |  |
| propanal + methylacrolein | 2,4-dimethylcyclopentanone | T | P |
|  | dimethylcyclopentadiene |  |  |
| acetoin + acetone | trimethylfuran | P | T |

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* H - Highly probable
P - Probable
T - Tentative

mechanism, our experiments showed that 2,4-dimethylcyclopentanone is a common product of both cellulose liquefaction and the reaction of propanal and methylacrolein. A general outline of the aldol condensation and the specific case of condensation between propanal and methylacrolein are both illustrated in Figure 1.

We are continuing studies to better understand the reactions involved in cellulose liquefaction. Also, we plan to study liquefaction of lignin and hemi-cellulose, which are other components of biomass. It is important to study the individual contributions of each of these three main components of biomass as well as their interactions to help us understand the liquefaction of available biomass resources to liquid fuels. The conversion products' potential for use as fuels is the topic of the next section.

## 3. PRODUCT USE AS AN ENERGY SOURCE

The liquid products of thermal degradation of cellulose in alkali contain up to 62% of the energy of the starting material even though they only contain a third of the mass. Of 26 experiments, the best case yielded acetone-soluble products that were 34% by weight of the initial cellulose. The heat of combustion of the product oil was 7500 cal/g (14,000 Btu/lb); the heat of combustion of cellulose is 4100 cal/g. Using these figures, the following calculation shows that 62% of the energy in the initial cellulose was concentrated in the product oil that was 34% of the initial cellulose mass:

$$\frac{7500\ \text{cal}}{\text{g oil}} \times \frac{\text{g cellulose}}{4100\ \text{cal}} \times \frac{34\ \text{g oil}}{100\ \text{g cellulose}} = 0.62 = 62\% \qquad 1$$

Table 2 lists the yields of acetone-soluble oil and the heats of combustion for the 26 experiments, in order of decreasing yields. Breaks in the table at 30% and 20% separate the experiments into three groups. Averages of these high, medium, and low yield groups summarize the mass yields, heats of combustion, and energy yields (see Table 3). (The mass and energy yields are the percentages of mass and energy in the initial cellulose that are contained in the acetone-soluble liquefaction products.) Though the average percent yields drop, the average heats of combustion remain relatively constant at 13,000 to 14,000 Btu/lb. Since the heat of combustion of cellulose is also constant, the energy yield is directly proportional to the mass yield as shown in Figure 2:

$$\%\ \text{Energy Yield} = \frac{\text{heat of comb. oil}}{\text{heat of comb. cell.}} \times \%\ \text{Mass Yield} \qquad 2$$

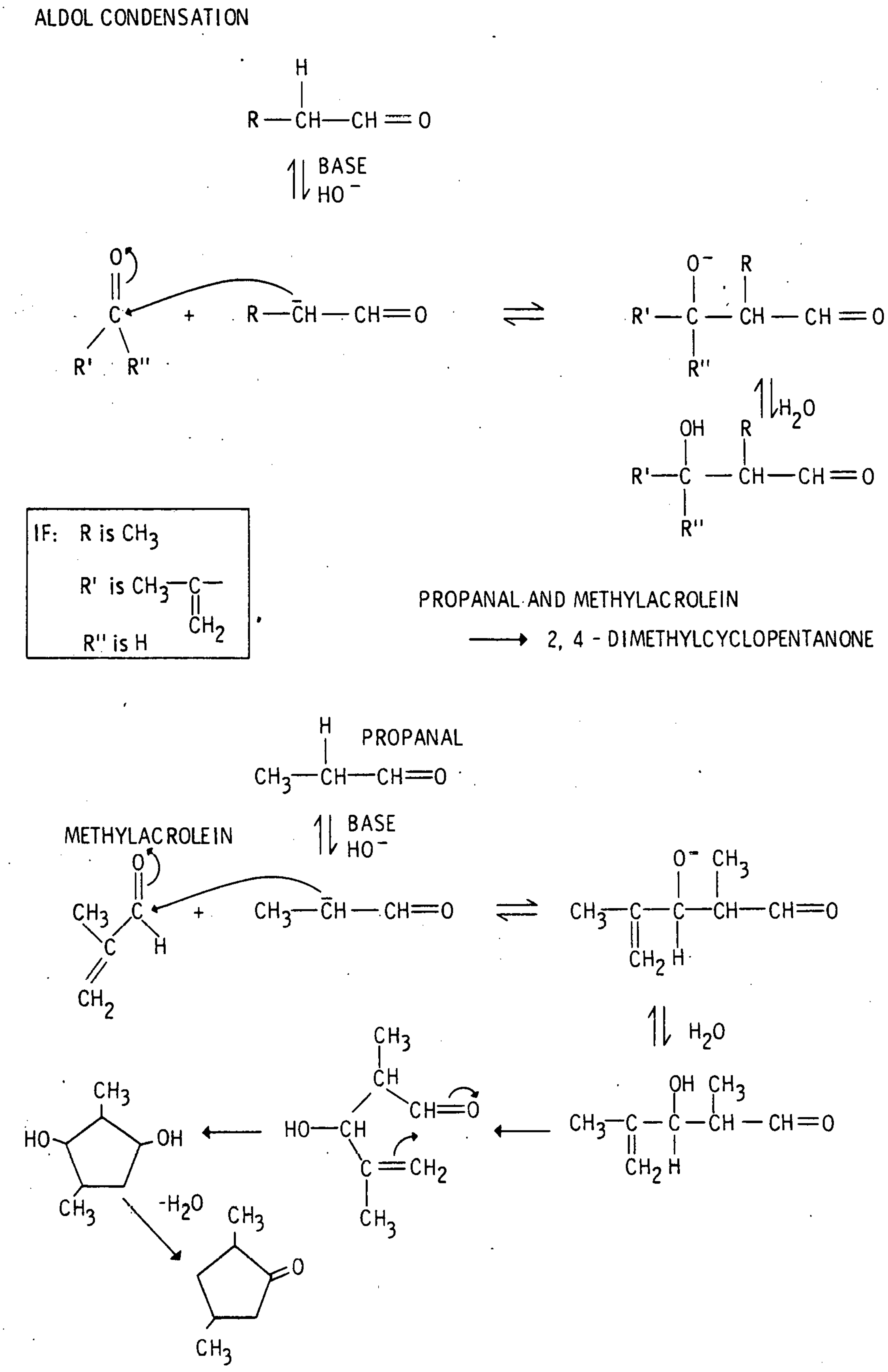

FIGURE 1. General and Specific Examples of the Aldol Condensation

TABLE 2. Mass Yields and Heats of Combustion for 26 Experiments[a]

| Experiment Number | % Mass Yield | Heat of Combustion (cal/g) |
|---|---|---|
| 110 | 34 | 7500 |
| 115 | 34 | 7200 |
| 113 | 33 | 7400 |
| 120 | 33 | 7600 |
| 107 | 31 | 7600 |
| 108 | 31 | 7300 |
| 117 | 31 | 7400 |
| 104 | 29 | 7900 |
| 125 | 29 | 7800 |
| 109 | 28 | 7600 |
| 112 | 28 | 8500 |
| 105 | 27 | 7700 |
| 118 | 27 | 7400 |
| 106 | 26 | 8800 |
| 128 | 26 | 7100 |
| 129 | 26 | 7700 |
| 122 | 24 | 8400 |
| 121 | 23 | 6000 |
| 126 | 23 | 7300 |
| 111 | 22 | 7600 |
| 123 | 21 | 8600 |
| 103 | 19 | 7400 |
| 119 | 15 | 7900 |
| 114 | 14 | 7300 |
| 127 | 11 | 8600 |
| 116 | 4 | 7800 |

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(a) Mass yield is the percent by weight of initial cellulose mass converted to acetone-soluble oil.

TABLE 3. Summary Comparing the Mass Yields with Heats of Combustion and Energy Yields

| | | Averages | | | |
|---|---|---|---|---|---|
| | | | Heat of Combustion | | |
| Group of Experiments | Number of Experiments | % Mass Yield | cal/g | Btu/lb | % Energy Yield |
| High Yield | 7 | 32 | 7400 | 13,000 | 58 |
| Medium Yield | 14 | 26 | 7700 | 14,000 | 49 |
| Low Yield | 5 | 13 | 7800 | 14,000 | 25 |

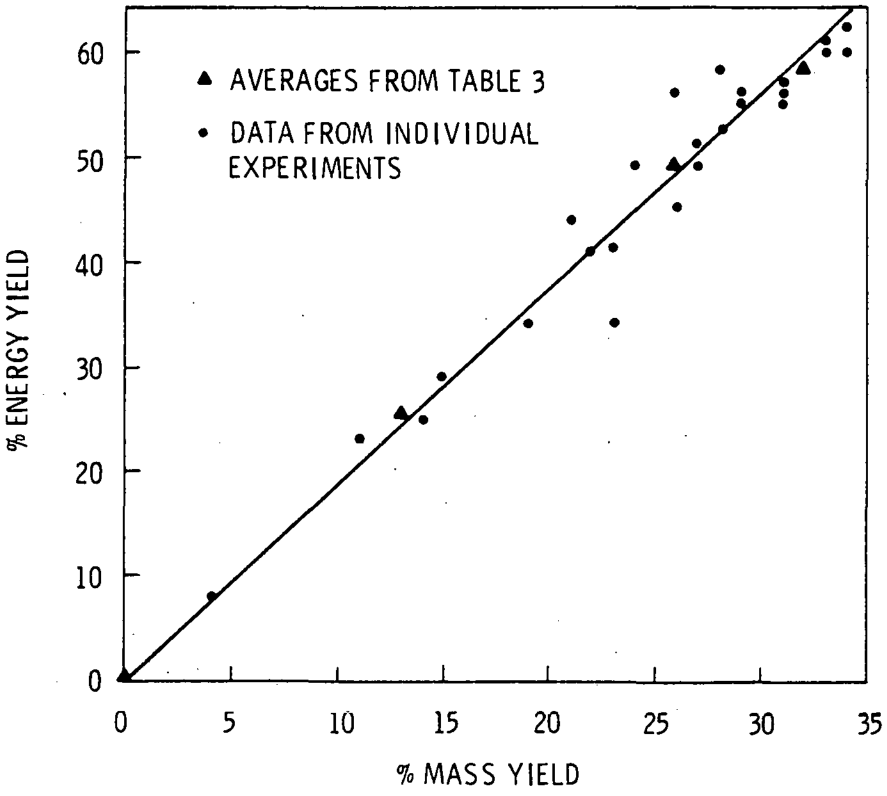

FIGURE 2. Energy Yield vs. Mass Yield

Over a wide range of reaction conditions, the mass yield varies considerably. While the energy yield varies directly in proportion to the mass yield, the amount of energy per unit mass, or heat of combustion, remains constant and is independent of reaction conditions. Specific effects of reaction conditions on liquefaction products are discussed in another publication (7).

Although in our basic research we have used pure cellulose, we have also liquefied peat moss, hops residue, and sewage sludge(a). In fact, any wet, finely divided biomass can be liquefied.

In work for the city and county of Honolulu, state of Hawaii, and the U.S. Environmental Protection Agency, we have liquefied municipal sewage sludge. For this example of liquefaction of actual biomass, the major products were synthetic asphalt, light oil, and residual char cake. A conceptual design for a sewage sludge liquefaction plant is shown in Figure 3. This design was developed to aid in determining the feasibility of continuing work beyond the laboratory-scale study conducted by PNL. The primary sludge from a wastewater treatment plant, dewatered to at least 30% solids, would be the feedstock. The light oil would be the main product for use outside the plant.

The plant in Figure 3 includes a section for solvent extraction of the char cake to produce a synthetic asphalt product. Depending on the value of

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(a) This information is reported by J. A. Russell, P. M. Molton and S. D. Landsman in "Chemical Comparisons of Liquid Fuels Produced by Thermochemical Liquefaction of Various Biomass Materials," presented at the 3rd Miami International Conference on Alternative Energy Resources.

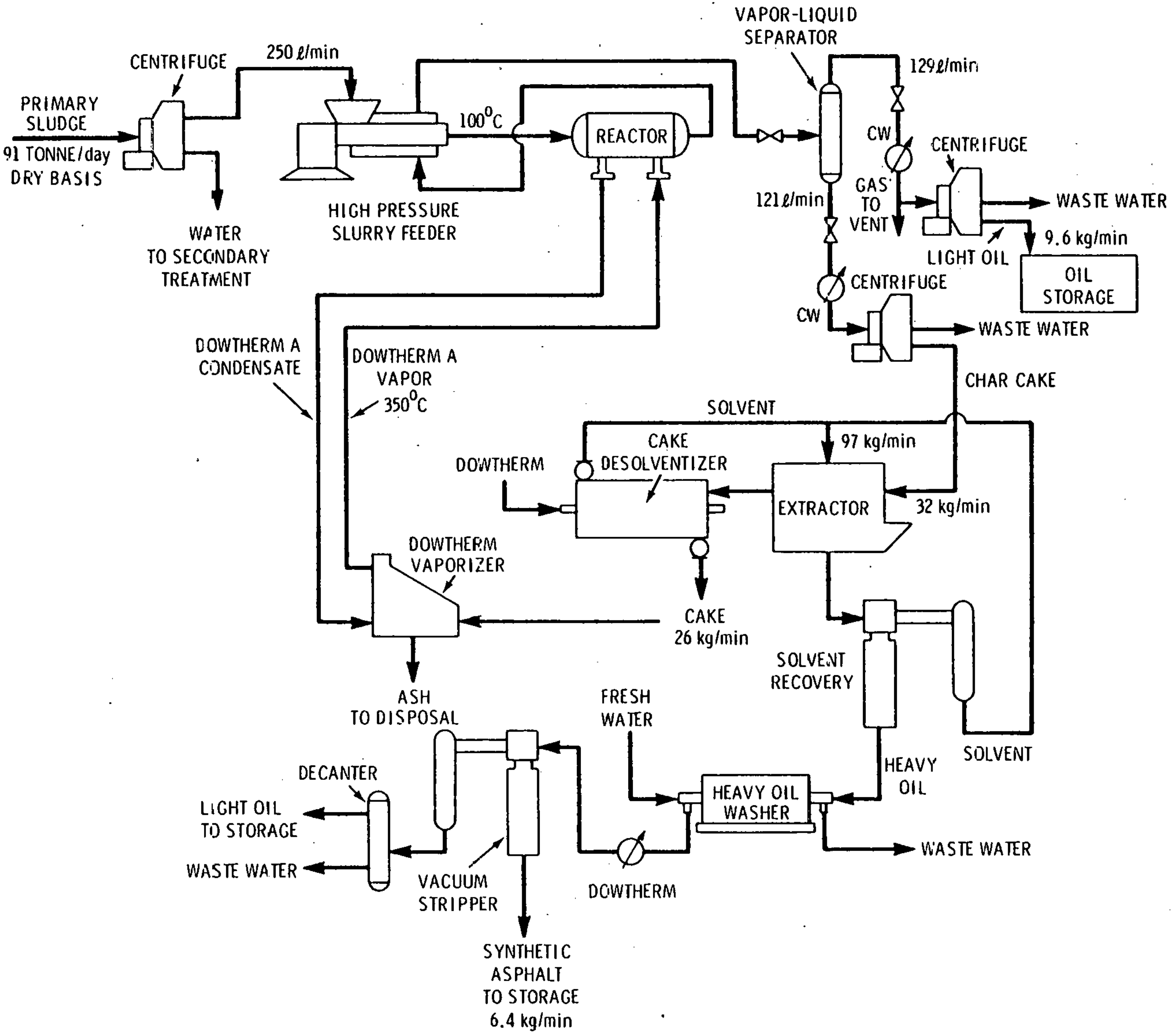

FIGURE 3. Preliminary Design for a Sewage Sludge Liquefaction Plant

the synthetic asphalt, this may or may not be desirable since solvent extraction requires additional capital and operating costs. As shown in Figure 3, the char cake is burned to produce process heat. Char cake burned at 80% efficiency will produce 1.56 x $10^{10}$J/h. Major heat requirements for liquefaction, desolventizing, and vacuum distillation total 1.54 x $10^{10}$J/h, so the process is self-sufficient in process energy requirements.

The liquefaction plant is envisioned to operate in conjunction with a municipal wastewater treatment plant. Economic feasibility of the process hinges on the credit taken for disposal of sludge (via liquefaction rather than landfill or other means) and on the price of petroleum products. Both of these are expected to escalate in future years.

## 4. SUMMARY

Biomass is a renewable energy resource that can produce liquid fuel by aqueous, alkaline, thermal degradation. However, before the liquid products can reasonably be used as fuels, further study is necessary to resolve problems such as high viscosity and the presence of corrosive compounds in the products. Our study of mechanisms will aid in process development by identifying appropriate feedstock, reaction conditions, and final products. Better understanding of the conversion technology's basic chemistry will help us use this resource more efficiently.

## ACKNOWLEDGMENTS

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