Macromol. Symp. ***135**, 205-214 (1998)*

Conversion of Polymers and Biomass to Chemical Intermediates with Supercritical Water

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Abstract: Recent results are described on conversion of polymers and biomass to chemical intermediates and monomers by using subcritical and supercritical water as the reaction solvent. Reactions of cellulose in supercritical water are rapid (<50 ms) and proceed to 100% conversion with no char formation. They show a remarkable increase in hydrolysis products and lower pyrolysis products when compared with reactions in subcritical water. Further, there is a jump in the reaction rate of cellulose at the critical temperature of water. If the methods used for cellulose are applied to synthetic polymers, such as PET, nylon or others, high liquid yields can be achieved although the reactions require about 10 min for complete conversion. The reason is the heterogeneous nature of the reaction system. For polyethylene, higher yields of short-chain hydrocarbons, higher alkene/alkane ratios and higher conversions were obtained in supercritical water than those obtained by pyrolysis.

INTRODUCTION

Recycling biomass and polymers for energy and resource conservation is an important future goal. For hydrolyzable materials, such as polymers derived from polycondensation reactions, some of the methods proposed include acid, basic, or enzymatic hydrolysis. For nonhydrolyzable materials, such as polymers derived from polyaddition reactions, main methods include pyrolysis. The focus of our work over the past few years (1-4) has been on conversion of biomass and polymers to chemical intermediates using high temperature and pressurized water as the reaction solvent. One of the advantages of water is that there is practically no char or carbon formation under hydrolytic or pyrolytic conditions, and frequently, reactions can be performed without catalysts. In this work, recent results on biomass and polymer conversion achieved in subcritical and supercritical water are presented.

A supercritical fluid is a substance that is above its critical point. Above the critical temperature of a substance, the gas can no longer be condensed to the liquid state regardless of the applied pressure. At temperatures and pressures just above the critical point, fluids acquire

CCC 1022-1360/98/$ 17.50

the properties that are intermediate to those of the liquid and gas. Transport properties such as viscosity and diffusion coefficients in the supercritical state are closer to gas-phase values. Densities and solvent loading capacities in the supercritical state are closer to liquid-phase values. Fugacities can be manipulated to cause increases or decreases in solubility, reaction rate and reaction equilibrium by orders of magnitude (5). Especially for water (T_c = 647.126 K, P_c = 22.055 MPa, ρ_c=0.322 g/cm^3), its properties vary dramatically as conditions change from the ambient to supercritical state. For example, at room temperature, the permittivity of water has a value of approximately 78 and water molecules easily solvate ionic species due to dipole interactions. Water provides reduction in Coulombic interactions between ions in solution due to its unusually high permittivity. As conditions are changed towards the critical point, the permittivity of water decreases and attains a value between 6 to 10, which is close to those of slightly polar organic compounds. This greatly affects the reaction rate and hydrocarbon solubility. Properties such as pH also undergo sharp changes (6,7). It should be apparent from the above that the properties of supercritical water can be manipulated to many advantages for chemical processing; these applications have been reviewed (8). The following sections describe some of the more interesting research on reactions in supercritical water, in particular those related to biomass and polymer recycling.

In the future, cellulose will be an important natural resource. Cellulose is a polymer that is made up of glucose units. The chemistry of the acid-catalyzed cellulose hydrolysis via the hydrolysis of $\beta(1 \rightarrow 4)$ glycosidic bonds and formation of short-chain cellulose polymers has been known to be one of the key steps (9). The reaction in supercritical water appears to be a method that allows a very rapid reaction. In our work (1-4), we have been able to hydrolyze cellulose in near-critical and supercritical water (T = 300-400 °C; P = 25-40 MPa) without using catalysts, with 100% conversions and without char or gas formation.

EXPERIMENTAL

Methods and materials

For biomass conversion, a flow arrangement, which we have found to be convenient, is shown in Fig. 1. Here, pure water is pressurized with pump 1 and preheated to the supercritical state and then mixed with reactants at ambient temperature, as a slurry or with another pump. After leaving the reactor, the mixture is brought to ambient conditions by direct injection of cooling water and with a heat exchanger. Particulate matter or solid product is removed by filtration and pressure is reduced with a back-pressure regulator. The residence time can be varied by changing the heated length of the reactor as well as by changing the reactant flow rate. Detailed kinetics have been examined as discussed below.

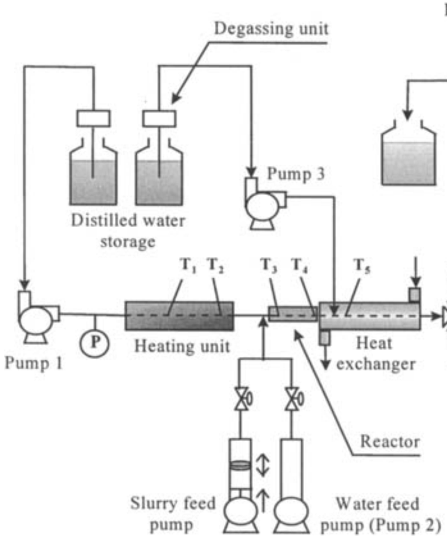

Figure 1. Flow apparatus for reacting cellulose slurries with subcritical and supercritical water

Because many of the polymers studied cannot be readily prepared in a slurry form, we have studied their reactions in subcritical and supercritical water using either a semibatch or batch-type apparatus. For semibatch experiments, the reactor is loaded with polymer and the reaction solvent at the desired temperature flows through the reactor. For batch experiments, a stainless-steel (SS 316) tube-bomb reactor (6 ml) equipped with an internal thermocouple was used.

Microcrystalline cellulose was used as a 1-5 wt.-% slurry. The hydrocarbon polymers used was low-density polyethylene (average molecular weight 68 000) and its model, hexadecane (98 %). The experiments were conducted under batch conditions in bomb reactors, with loading water densities ranging from 0.1 to 0.42 g/cm^3, as described above. The pressure in the reactor for experiments using water was estimated from temperature and density data (10). The experiments were also conducted without water and in an argon atmosphere. The reaction time was 30 min. In the polyethylene experiments, the products were first fractionated into THF-soluble and THF-insoluble products.

RESULTS AND DISCUSSION

Cellulose

Figure 2 shows HPLC chromatographs for 100% conversion of cellulose in subcritical and supercritical water. It is apparent from the figures that higher yields of hydrolysis products are achieved in supercritical than in subcritical water, i.e., for 100% conversion of cellulose, more pyrolysis products are produced in subcritical water.

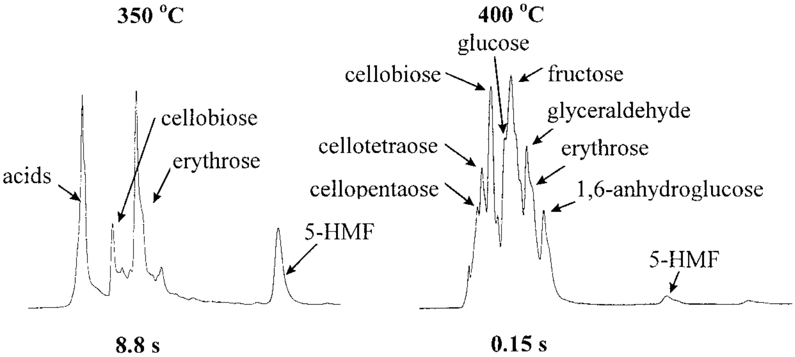

Figure 2. HPLC analyses for 100% cellulose conversion in water at 25 MPa: (a) subcritical, (b) supercritical conditions. (5-HMF = 5-hydroxymethyl-2-furaldehyde)

Figure 3 shows the results for the decomposition of cellulose and its model compounds, cellobiose and glucose, in supercritical water studied under flow conditions, where apparent rate constants are plotted versus inverse temperature.

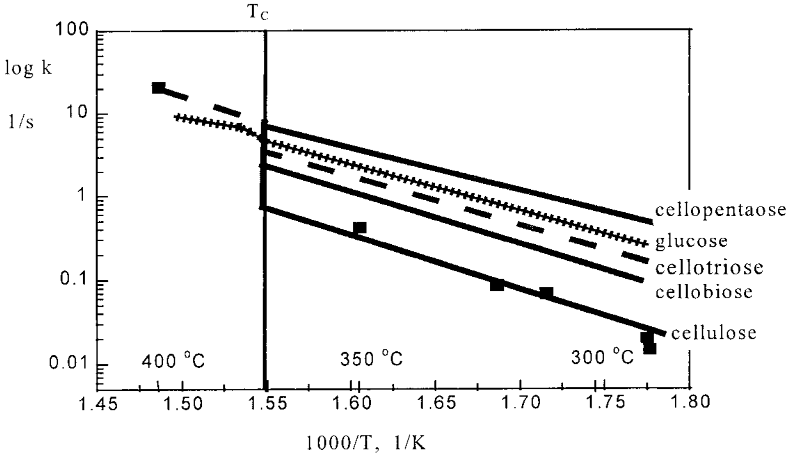

Figure 3. Arrhenius plot of apparent rate constants of hydrolysis of cellulose and model compounds in sub- and supercritical water

The results show that the kinetics of cellulose hydrolysis undergo a jump to unprecedented higher hydrolysis rates as the conditions change from sub- to supercritical water. The products are mainly water-soluble oligomers, glucose, fructose and decomposition products of glucose. For temperatures below the T_c of water, the glucose decomposition rate constant is higher than that for cellulose. However, at temperatures above the T_c, the rate constant is lower than that of cellulose. This is why high yields of hydrolysis products were obtained; we believe that this phenomenon is due to the phase behavior of the cellulose - water system. We have studied the reaction of cellulose model compounds (cellobiose, cellotriose, cellopentaose, etc.) in detail to elucidate the reaction pathways and kinetics of these compounds in sub- and supercritical conditions. For example, the reaction pathway of cellobiose was elucidated (3). The kinetics of each pathway were evaluated for a number of substances (11,12) and cellulose decomposition has been successfully modelled with a Monte Carlo simulation techniques.

Cellobiose

On the basis of HPLC analyses and numerous experiments, the reaction pathway of cellobiose was elucidated as shown in Fig. 4. Cellobiose undergoes parallel reaction via hydrolysis (k_H) to form glucose and pyrolysis (k_1, k_2) to form the products, glucosyl-erythrose (GE) and glucosyl-glycolaldehyde (GG). Pyrolysis only occurs at the reducing end of the molecule and hydrolysis only on glycosidic bonds. GG and GE hydrolyzed ($k_{H,GG}$ and $k_{H,GE}$) to form glucose plus glycolaldehyde and glucose plus erythrose, respectively. The glucose formed undergoes further decomposition (k_G) to other products. This information is used to improve the simulation of cellulose decomposition.

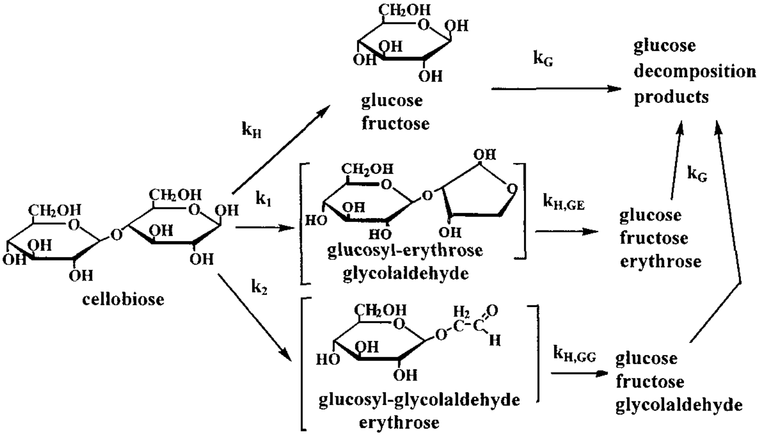

Figure 4. Reaction pathways for cellobiose

Synthetic polymers

Conversion of the polymers to intermediates or monomers may require special techniques because of a wide range of structures and reactivities. In our work, we have found that condensation polymers, such as poly(ethylene terephthalate) (PET), polyurethane and various Nylons can be converted to intermediates or monomers at conversions approaching 100 % and with only few gaseous products.

Poly(ethylene terephthalate)

The results of the decomposition of poly(ethylene terephthalate) (PET) in supercritical water are shown in Fig. 5. The reaction primarily produced its monomers, terephthalic acid and ethylene glycol. Formation of other products such as benzoic acid, benzene, acetic acid and carbon dioxide was negligible under the present conditions, due to further decomposition or decarboxylation. Consequently, little or no gaseous products were formed in these reactions.

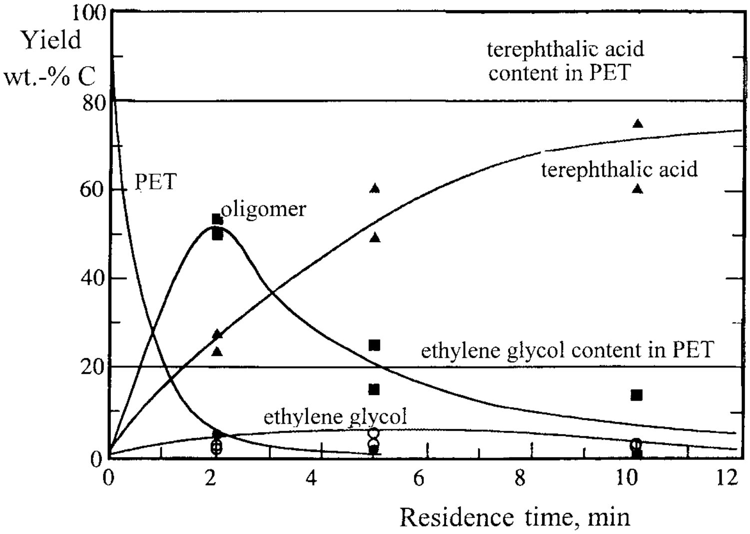

Figure 5. PET conversion in supercritical water (400 °C, 40 MPa)

Nylon and other polymers

We examined batch and semibatch conversions of polymers such as lignin, chitin, chitosan, silk, Nylon, PET, polyurethane, and others shown in Table 1. As expected, polymers containing ether, ester or amide bonds could be decomposed in supercritical water in 1-30 min. Polymers derived from polyaddition reactions, such as polyethylene or polypropylene, reacted slowly as expected. In the next section, we examine product distribution for these polymers in the presence of water.

Table 1. Decomposition of polymers with supercritical water (T=400 °C, $\rho(H_2O)$ =0.5 g/cm^3)

Reactant	Bond Cleaved	Reaction time, min	Conversion, %
Cellulose	C-O	1	100
Chitin	C-O	1	100
Chitosan	C-O	1	100
Silk	CO-NH	1	100
Nylon 66	CO-NH	5	98+
PET bottles	CO-O	5	100
Polyethylene	CH_2-CH_2	30	12
Wood	C-O, C-C	1	78
Lignin	C-O	1	90

Hexadecane - model compound

Since hexadecane is miscible with supercritical water (13), the reaction mixture is homogeneous. As alcohols, carboxylic acids, and carbon dioxide were not detected in the products, the main reaction of the *n*-alkane decomposition under the present experimental conditions is considered to be pyrolysis, even in supercritical water. The product distribution and 1-alkene/*n*-alkane ratios obtained for each case were practically the same. The hexadecane first-order rate constant obtained in the presence of supercritical water was not significantly different from that obtained for pyrolysis in an argon atmosphere. In general, the role of supercritical water in a reaction might consist in cage effect, water attack on the reactant or its thermolysis, a rate or equilibrium change due to variation of permittivity, and change in the phase behavior (14). However, under the present conditions, the effect of supercritical water on the hexadecane decomposition was negligible.

Polyethylene

For addition polymers, such as polyethylene or polypropylene, the reaction in supercritical water was slow. For these polymers, thermal cracking is a well- known conversion technique to recover oils (15,16). The control of product distribution in the pyrolyzed oils is considered to be an important technical factor for practical recycling. Pyrolysis in the presence of a solvent may be a method of controlling the product distribution as reported in studies on cracking of heavy oil or its model compounds (17,18). Reaction temperature is frequently above 673 K, which is well above the critical temperature of most applicable solvents. Therefore, we employed supercritical water as a reaction solvent for chemical cracking of these plastics expecting control of the product distribution.

Pyrolysis of polyethylene is considered to proceed mainly in the melt, and thus the reaction conditions are totally different from those of the hexadecane pyrolysis. Figure 6a shows the product distribution for lighter products (gas and THF-soluble products). The yields of short-chain hydrocarbons increased with increasing water density, which shows that polyethylene pyrolysis is enhanced in supercritical water. As shown in Fig. 6b, the 1-alkene/*n*-alkane ratio for the light products also increased with increasing water density.

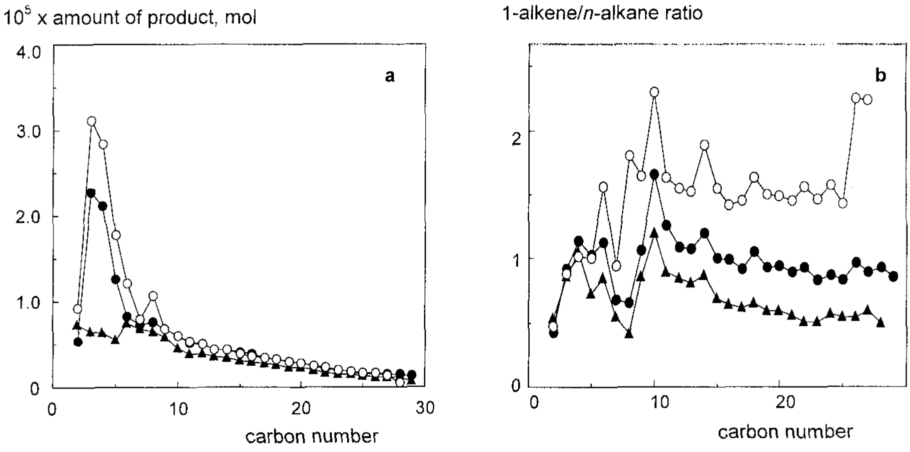

Figure 6. Product distribution for the pyrolysis of polyethylene at 693 K and 30 min reaction time. Symbols: ▲ in argon (0.1 MPa); ● in supercritical water, ρ=0.13 g/cm^3; O in supercritical water, ρ=0.42 g/cm^3.

Thus, polyethylene pyrolysis in supercritical water is obviously different from that in argon; the differences could not be observed for the hexadecane pyrolysis. This seems to be due to the difference in performing the reaction, i.e., homogeneous reaction in the case of hexadecane and heterogeneous reaction in the case of polyethylene. In argon atmosphere, pyrolysis of polyethylene mainly occurs in the molten polymer. On the other hand, supercritical water can dissolve some lighter hydrocarbons produced from pyrolysis. Therefore, pyrolysis of these hydrocarbons in the supercritical phase affects the product distribution. Also, some water is considered to dissolve in the molten polymer phase, which dilutes the phase and influences the pyrolysis. The chemistry of this phenomenon is currently under investigation.

CONCLUSION

Conversion of biomass and polymers using subcritical or supercritical water is an effective method, especially for condensation polymers. High conversions, up to 100 %, can be obtained with low gas yields and little or no char formation. For addition polymers, the conversion is more difficult. Almost the same product distribution and conversions were obtained for reaction of hexadecane in supercritical water and for its pyrolysis under argon. For polyethylene, product distribution and conversion were greatly influenced by water, higher yields of short-chain hydrocarbons, higher alkene/alkane ratios and higher conversions being obtained in supercritical water than in pyrolysis. These differences can be explained by the heterogeneous nature of the reaction.

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