SUPERCritical EXTRACTION OF USED AUTOMOTIVE TIRE WITH WATER

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Samples from a used automotive tire were subjected to subcritical and supercritical extraction with water. Supercritical water was found to be almost as effective as supercritical *n*-pentane. For a 9-mm cube sample the rate of supercritical extraction with water followed a first-order kinetics with an activation energy of 170 kJ/mol. Dynamic TGA data for 0.13–0.35 mm samples showed that pyrolysis at temperatures of 690–730 K had almost the same activation energy as did supercritical extraction with water.

Introduction

Supercritical extraction, which has been popular in the food processing industry, is recently gaining attention in the field of oil recovery from low-rank coal or coal liquefaction; toluene has been widely employed as a solvent for the supercritical liquefaction of low-rank coal.^{1–5,7,11–14,19} However, Barton⁶ performed supercritical liquefaction of coal in the environment of a mixture of water, hydrogen and catalyst. Deshpande *et al.*⁸ studied liquefaction of coal, lignite and glucose with supercritical water. Towne *et al.*¹⁸ also studied coal liquefaction in supercritical aqueous mixtures containing tetrahydroquinoline, quinoline or tetralin. Also, various patents describe the use of supercritical water for coal,^{15,17} oil shale¹⁶ and tar sand.¹⁵ One disadvantage of using water as a solvent is that its critical pressure is high. However, the easy separation of water from oil extracted as well as the negligible cost of the solvent may be great advantages.

In this work a used automotive tire is subjected to subcritical and supercritical extraction with water. The data are then compared with those obtained in previous work⁹ from extraction with *n*-pentane, toluene and nitrogen under the subcritical and supercritical conditions. Also, the samples are tested in a dynamic thermogravimetric analysis. The samples used in this work are from the same batch used in the earlier work.⁹

1. Experiments

1.1 Extraction

The samples were from an undertread part of a

used automotive tire. An autoclave of 0.7 liters was used as a batch reactor. The experimental conditions and the composition of the samples are listed in **Table 1**. The experimental techniques were identical with those of the previous work:⁹ Approximately 1 g of the 9-mm cube sample was loaded into a stainless steel basket suspended in the autoclave. Air in the autoclave was removed by a vacuum pump and then water was introduced. The amount of water introduced ranged from 45–200 g, depending on the experimental conditions of pressure and plateau temperature. To attain the conditions of 23 MPa and 653 K, for example, 140 g of water was charged to the autoclave. The space around the basket was agitated with an 800-rpm stirrer. The autoclave was externally heated at a rate of 0.1 K/s until it reached an intended temperature and then was maintained at this plateau temperature. The autoclave's pressure gauge showed little change in pressure during each extraction. Also, several preliminary runs with a 600-rpm agitator showed that the same sample weight decrease-time curve was obtained as that with 800 rpm.

At a certain extraction time the autoclave was quickly cooled. The residual solid was taken out, dried and weighed. The oil extracted was also recovered by cleaning the autoclave with tetrahydrofuran solvent. The solvent was then evaporated. A fresh sample was again placed in the stainless steel basket for the measurement of solid weight decrease at a longer extraction time.

1.2 Pyrolysis

Thermogravimetric analyses of fine particles of the tire sample were carried out in a Dupont 951 TGA. A sample, in a large piece frozen in liquid nitrogen, was crushed and ground and then sieved. The fine par-

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Table 1. Composition of tire sample and experimental conditions for extraction

Sample:	Undertread part of a used tire		
Component	Weight	%	
Natural rubber	80	52.2	
Styrene-butadiene rubber	20	13.0	
Carbon black (HAF)	45	29.4	
Zinc oxide	5	3.3	
Sulfur	3.2	2.1	
Additives (small amount)			
Sample size:	Cube $9 \times 9 \times 9$ mm		
Solvent:	Water		
Temperature and pressure:			
Plateau temperature, T , K	603–723		
Pressure, P [MPa]	5.2–23		
<hr/>			
Critical temperature, T_c , K	647		
Critical pressure, P_c , MPa	22.0		
Reduced temperature, T/T_c	0.932–1.12		
Reduced pressure, P/P_c	0.24–1.05		

ticles (about 10 mg of size = 0.13–0.35 mm) were placed in a sample holder and pyrolyzed in a nitrogen stream at a flow rate of 1.3 ml/s and a heating rate of 0.17 K/s.

Pyrolysis experiments with a 9-mm cube sample were also carried out in the autoclave in the nitrogen environment. Experimental procedures for the pyrolysis were identical with those for the supercritical extraction.

1.3 Analyses

Elementary analyses of the solid residue and oil extracted were performed by burning the sample in a stream of oxygen: Sulfur by absorption of SO₂ in a H₂O₂ aqueous solution followed by titration with Ba(NO₃)₂ solution, carbon by absorption of CO₂ in solid NaOH, and hydrogen by absorption of H₂O in magnesium perchlorate anhydride.

Average molecular weights of the oil extracted were measured by a vapor pressure osmometer, Hitachi model 115, using benzene solvent and benzil as a standard.

2. Results

2.1 Extraction

Figure 1 shows the solid weight vs. time data at 653 K. It is clear that the weight decreases more rapidly at supercritical pressure 22+ MPa than at subcritical 5.2 MPa, but the weights go down in both cases to almost the same limiting value when the extraction is completed.

The data⁹⁾ obtained from extraction with toluene, *n*-pentane and nitrogen are also included in Fig. 1. It is an interesting finding that supercritical water is almost as effective as supercritical *n*-pentane, although the supercritical pressure of water is an order of magnitude higher than that of *n*-pentane (critical

Fig. 1. Weight decrease of 9-mm cube rubber sample in subcritical and supercritical extraction with water; data⁹⁾ obtained from extraction of 9-mm cube sample with toluene, *n*-pentane and nitrogen.

pressure = 3.37 MPa).

If the rate of decrease in solid weight, *W*, is assumed to be of first order:

$$-\frac{dW}{dt} = k(W - W_{\infty}) \quad (1)$$

where *W_∞* is the weight at the extraction completion, and *k* is the overall rate constant.

The integration of Eq. (1) at constant temperature gives

$$\ln \frac{W - W_{\infty}}{W_1 - W_{\infty}} = -k(t - t_1) \quad (2)$$

where *t₁* is the time when the autoclave temperature reaches a prescribed temperature, and *W₁* is the solid weight at time *t₁*.

It is found from Fig. 1 that the residual solid weight at the extraction completion, *W_∞/W₀*, is little affected by pressure in the range of 5–22 MPa. **Figure 2** shows a temperature dependency of *W_∞/W₀* measured in the range 623–723 K. At 653 K the weight reaches the limiting value in 72 hours, at 723 K in about 3 hours.

From the limiting values of *W_∞/W₀* and the sample composition listed in Table 1 it is clear that the solid residue at the extraction completion consists of not only carbon black, zinc oxide and sulfur (as discussed later) but also a solid carbonized from the rubber material itself.

With these *W_∞/W₀* data the overall rate constants *k* for supercritical extraction are evaluated from Eq. (2). The rate constants are then plotted in terms of ln *k* vs. 1/*T* in **Fig. 3**. Except for some points deep in the subcritical region the rate constants of supercritical extraction are well expressed by an Arrhenius-type equation with an activation energy of 170 kJ/mol. Also, note that the solid line drawn in Fig. 1 is a

Fig. 2. Effect of temperature on solid residue weight at completion of extraction.

Fig. 3. Arrhenius plots of rate constants of extraction; those of dynamic TGA.

theoretical line calculated from Eq. (2) with the values of k and W_{∞} .

Table 2 presents some typical results obtained from analyses of the solid residue and oil extracted with water at extraction time 5.5 hours (including 1-h temperature rise period). The overall mass balance is only 90.5%, but it indicates roughly that about 48 wt% of the tire sample turns to oil and 43 wt% to solid residue. The elementary analyses show that the oil consists of 86 wt% carbon, 10% hydrogen and 2% sulfur; 92% of the solid residue is carbon and 2% is sulfur. So about half the sulfur contained in the original sample is extracted into the oil and the other half remains in the solid residue. The chemical analysis data of the solid and oil extracted with *n*-pentane and toluene in the previous work⁹⁾ are also included in Table 2. It is interesting that the composition of oil extracted and that of solid residue are little affected by supercritical solvent, whether water, *n*-pentane or toluene.

Houser *et al.*¹⁰⁾ found that under certain conditions nitrogen- and/or sulfur-containing organic compounds react with supercritical water and lighter hydrocarbons are produced. In our experiments, as depicted in Table 2, the overall mass balance of the extraction with supercritical water is low compared to the previous experiments with toluene and *n*-pentane.

Table 2. Chemical analyses of residual solid and oil extracted

Extraction conditions			
Solvent	Water	<i>n</i> -Pentane ^f	Toluene ^f
Plateau temperature, K	653	653	653
Pressure, MPa	22+	5.2	5.2
Time (including 1-h temperature-rise period), h	5.5	5.5	5.5
Oil extracted			
Yield ^a	47.6	48.1	56.7
C, wt% ^b	85.6	85.1	86.5
H, wt% ^b	10.0	10.2	9.79
S, wt% ^b	2.08	2.10	2.10
Atomic H/C	1.39	1.43	1.35
Yield of isoprene recovered ^c	—	?	0.65
Solid residue			
Yield ^d	42.9	47.4	39.7
C, wt% ^e	91.6	92.1	92.9
H, wt% ^e	1.48	1.90	0.85
S, wt% ^e	2.07	1.94	1.86
Atomic H/C	0.19	0.25	0.11
Balances			
Total mass, wt%	90.5	95.5	97.1
C, wt%	90.6	95.8	98.0
H, wt%	81.0	87.2	89.6
S, wt%	89.4	91.9	91.9

Original sample: C=88.3; H=6.66; S=2.10; Atomic ratio (H/C)=0.899.

^a (mass of oil extracted)/ $W_0 \times 100$.

^b (mass of element)/(mass of oil extracted) $\times 100$.

^c (mass of isoprene recovered)/ $W_0 \times 100$.

^d (mass of solid residue)/ $W_0 \times 100$.

^e (mass of element)/(mass of solid residue) $\times 100$.

^f from Funazukuri *et al.*⁹⁾

This may be partly due to reaction of the rubber material with supercritical water; the lighter species produced would have stripped off when the oil extracted was recovered by evaporating the solvent, tetrahydrofuran.

Figure 4 shows the time dependency of the solid weight decrease and the average molecular weights of the oil extracted with water at 653 K and 22+ MPa. As depicted, no more solid weight decrease is observed after 4 hours, while the average molecular weight keeps decreasing over the entire 13-hour period of the measurements. This is an indication of further decomposition of the extracted oil in the batch reactor.

The average molecular weight of the oil extracted with water at 653 K and 22+ MPa till extraction time 5.5 hours (including 1-h temperature rise period) is 320, which is also similar to those (325–480) obtained with *n*-pentane and toluene.⁹⁾

2.2 Pyrolysis

The TGA thermogram measured is shown in Fig. 5. A sharp decrease in solid weight is observed at temperatures 700–730 K. Separate experiments performed in a stream of nitrogen at various constant

Fig. 4. Average molecular weight of oil extracted and weight decrease of 9-mm cube rubber sample in supercritical extraction with water at 653 K and 22+ MPa.

Fig. 5. Thermogram of TGA.

temperatures show that the solid weight decreases slowly at lower temperatures. The solid weight decreases to a limiting value, W_{∞} , at 723 K in only 3 hours, while at 593 K the limiting weight is attained in 111 hours. However, as shown in Fig. 6, almost the same limiting weight, $W_{\infty}/W_0 = 0.40$, is obtained over the temperatures 593–723 K.

The pyrolysis data shown in Fig. 5 are analyzed on the basis of an equation of the same type as Eq. (1). With a W_{∞}/W_0 value of 0.40 the rate constants k_{pyro} are evaluated from Eq. (1) with a differentiation of the TGA curve and the weight decrease, $W - W_{\infty}$, at each temperature. The rate constants k_{pyro} thus obtained are included in Fig. 3.

3. Discussion

Figure 3 shows that the k_{pyro} values at high temperatures (690–730 K) lie on a straight line with an activation energy of 160 kJ/mol. Also, this straight line falls almost on an extension of the line for supercritical extraction with water. About half the weight decrease resulting from thermal decomposition is observed in this range of high temperature. The fact that the activation energy of the supercritical

Fig. 6. Effect of temperature on solid residue weight at completion of thermal decomposition.

extraction with water is almost the same as that of the dynamic TGA at temperatures 690–730 K suggests that thermal decomposition would also be an intrinsic process of supercritical extraction at these high temperatures.

The rate of TGA at the temperatures 690–730 K for fine particles is expressed by a first-order equation. The data of the supercritical extraction with water for 9-mm cube samples are also correlated by a first-order equation. Figure 7 shows the solid weight–time curve measured in supercritical extraction with water at 22+ MPa and 653 K, and those in pyrolysis in a nitrogen environment at 0.2 MPa and temperature in the range of 563–653 K. These supercritical extraction and pyrolysis data are obtained with 9-mm cube samples in the batch autoclave. It is found that the solid weight at the pyrolysis completion decreases with increasing temperature. Also, in supercritical extraction more weight decrease is observed at the extraction completion and, as shown in Fig. 2, the solid weight W_{∞} is less affected by temperature than in pyrolysis.

In both supercritical extraction and pyrolysis the thermal decomposition is considered to be the prime reaction taking place in the solid sample. The fact that as far as the 9-mm cube sample is concerned the supercritical extraction is of first order and the pyrolysis is not is considered to occur because under supercritical conditions intraparticle mass transfer processes become fast and the controlling step is the thermal decomposition, while in pyrolysis the overall reaction is controlled by thermal decomposition only when the solid is as small as powder. This agrees with the experimental result of the previous work⁹⁾ that the rate constant of extraction with *n*-pentane depends upon particle size (9 mm and 3.5 mm) when the pressure is subcritical, but no longer depends on the size when the pressure becomes supercritical.

4. Conclusion

1. Supercritical extraction of a used automotive tire with water showed that supercritical water was almost as effective as supercritical *n*-pentane.
2. The rate of supercritical extraction with water followed a first-order kinetics with an activation

Fig. 7. Weight decrease of 9-mm cube rubber sample in pyrolysis at 563–653 K and a nitrogen atmosphere of 0.2 MPa; in supercritical extraction with water at 653 K and 22 + MPa. Time includes a transient period in which temperature is raised at 0.17 K/s from 293 K to prescribed temperature.

energy of 170 kJ/mol.

3. Dynamic TGA data showed that the pyrolysis at temperatures 690–730 K had almost the same activation energy as the supercritical extraction with water.

Nomenclature

k	= extraction rate constant	$[s^{-1}]$
k_{pyro}	= pyrolysis rate constant	$[s^{-1}]$
t	= time	$[s]$

t_1	= time when autoclave reaches a prescribed temperature	$[s]$
W	= solid weight	$[kg]$
W_0	= initial weight of sample	$[kg]$
W_1	= solid weight at time t_1	$[kg]$
W_{∞}	= solid weight at extraction/pyrolysis completion	$[kg]$

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