π_s = dimensionless pressure at stagnation point [—]
 ϕ = bank contact angle [deg]

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SUBCRITICAL AND SUPERCRITICAL EXTRACTION OF OIL FROM USED AUTOMOTIVE TIRE SAMPLES

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Samples from a used automotive tire were subjected to sub- and supercritical extraction with *n*-pentane, toluene and nitrogen. Solvent effectiveness for extraction was greatest for toluene and least for nitrogen. When the extraction with toluene was completed at temperature 653 K and pressure 5.2 MPa, for instance, 57% (by weight) of the sample was converted to liquid oils and 40% remained as solid residue. Rate constants for extraction with *n*-pentane, assuming that the process is first-order, increase with both temperature and pressure. Scanning electron microscope pictures show that many cavities are produced inside the solid during extraction with toluene and *n*-pentane. From this evidence a qualitative explanation of the process is suggested.

As described in an extensive review by Williams,⁷⁾ supercritical extraction has been increasingly popular in many chemical and food processing industries. In the past few years, it has been applied to the field of oil recovery from fossil fuels such as coal,^{1,2,4)} oil shale⁴⁻⁶⁾ and tar sand.^{4,6)} The purpose of this study is to assess the applicability of sub- to supercritical extraction for the recovery of oil from used automotive tires. The extraction was carried out with toluene, as an aromatic solvent, and *n*-pentane, as an

aliphatic solvent, and also with nitrogen.

1. Experimental Apparatus

The tire samples were small cubes of two different sizes, 3.5 mm and 9 mm, cut from the undertread part of the tire. **Table 1** lists the compositions of the samples used for the extraction experiments.

Approximately 1 g of the sample (one 9-mm cube or 17 3.5-mm cubes) was loaded into an aluminium basket suspended with a wire in a one-liter autoclave. Air in the autoclave was removed by means of a vacuum pump and then the organic solvent (*n*-pentane or toluene) or nitrogen gas was introduced.

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Table 1. Experimental conditions

Sample: Composition of used tire samples			
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: 3.5 × 3.5 × 3.5 mm and 9 × 9 × 9 mm			
Temperature and pressure:			
	<i>n</i> -Pentane	Toluene	Nitrogen
Plateau temperature, T, K	563–653	653	653
Pressure, P, MPa	0.3–5.2	5.2	0.2, 5.2
<hr/>			
Critical temperature*, T _c , K	470	592	126
Critical pressure*, P _c , MPa	3.37	4.11	3.39
Reduced temperature, T/T _c	1.20–1.39	1.10	5.18
Reduced pressure, P/P _c	0.09–1.54	1.27	0.06, 1.53

* From literature.³⁾

The space around the basket was agitated with an 800-rpm stirrer. By monitoring the temperatures measured with a thermocouple inserted in this space, the autoclave was heated by an external heating element at a rate of 0.1 K/s until it reached a prescribed temperature. The autoclave was then maintained at this plateau temperature.

The experimental conditions of temperature and pressure are also listed in Table 1. The pressure depended upon the amount of liquid solvent or gas admitted to the autoclave.

2. Experimental Results

2.1 Effect of solvent

Figure 1 shows the residual solid weight vs. time curves (in terms of W/W_0 vs. t , where W is the weight at time t and W_0 is the weight at time zero) experimentally measured for the extraction of 9-mm cube samples. Data are given for *n*-pentane and toluene at 653 K and a pressure of 5.2 MPa, and for nitrogen at the same temperature and at pressures of 0.2 MPa and 5.2 MPa. In the transient period, the temperature increased at a constant rate of 360 K per hour so that the autoclave, initially at room temperature, 293 K, reached the plateau temperature, 653 K, in 1 h. In Fig. 1, each point was obtained with a separate sample. At the prescribed time the autoclave was quickly opened (after releasing the gas, but not cooling down the autoclave), and the solid residue was taken out, dried (in the case of the extraction with *n*-pentane and toluene), and weighed to determine W/W_0 .

Table 2 lists the weight decrease, $1 - (W/W_0)$, and the weight decrease rate, $r = -d(W/W_0)/dt$, at the termination ($t = 1$ h) of the transient period. The rate

Fig. 1. Weight decrease of 9-mm cube rubber sample, in supercritical extraction with *n*-pentane, toluene and nitrogen at 653 K; subcritical extraction with nitrogen at the same temperature.

Table 2. Weight decrease during transient (temperature-rise) period of 1 h; weight-decrease rate at time when temperature reaches plateau, 653 K

Sample size: 9-mm cube
Plateau temperature: 653 K
Pressure: 5.2 MPa

	<i>n</i> -Pentane	Toluene	Nitrogen
$1 - (W/W_0)$ at $t = 1$ h	0.20	0.30	0.03
Ratio with respect to nitrogen	6.7	10	1
<hr/>			
$r = -\frac{d(W/W_0)}{dt}$ at $t = 1$ h, 1/s	1.1×10^{-4}	3.8×10^{-4}	4.6×10^{-5}
Ratio with respect to nitrogen	2.4	8.3	1

values were obtained by graphical differentiation of the curves in Fig. 1. The $1 - (W/W_0)$ data at this pressure show that the sample weight decreases only by 3% with nitrogen during the transient period of 1 h, while the weight decrease with *n*-pentane is 20% and that with toluene is 30%. When the nitrogen pressure is 0.2 MPa, the weight decrease is but 1.5% during this transient period. The ratios in terms of $1 - (W/W_0)$ and r , both at $t = 1$ h, listed in Table 2 also show that toluene is the most effective solvent.

Figure 1 also shows that when extraction is completed, W/W_0 with *n*-pentane becomes 0.41 (59% extracted) and that with toluene falls slightly below 0.40.

2.2 Oil products

The oil produced at an extraction time of 5.5 h was recovered first by quickly cooling the autoclave with air and water. Then it was opened and the solvent (in the case of toluene and *n*-pentane) plus dissolved oil

Table 3. Typical mass balances

Sample size: 9-mm cube			
	<i>n</i> -Pentane	Toluene	Nitrogen
Plateau temperature, K	653	653	653
Pressure, MPa	5.2	5.2	5.2
Time elapsed (including the temperature-rise period of 1 h), h	5.2	5.5	5.5
Yield, wt%			
Solid residue	47.4	39.7	59.8
Oils recovered	48.1	56.7	38.9
Isoprene recovered	?	0.65	1.21
Total	95.5+?	97.1	99.9
Average molecular weight of oil product	480	325	370
Sulfur content of oil, wt%	2.1	2.1	2.2

and solid residue were recovered. Besides dissolved oil, there was some oil adhering to the inside walls of the autoclave. This material was recovered by introducing toluene in the autoclave and heating to 653 K at 5.2 MPa. In the case of nitrogen, the extracted oil was recovered only in this toluene solution.

Together with the oil, isoprene produced in the extraction was dissolved in the solvent. The amount of isoprene produced was then determined by a gas chromatograph (Shimadzu model 7AGC (both FID and TCD); stainless steel column of 2 mm i.d. and 2 m long packed with 80/100 mesh Porapak QS; He carrier gas at 50 ml/min; 60°C for 2 min, thereafter rising at 8°C/min up to 200°C). However, in the case of *n*-pentane, the isoprene could not be analyzed because isoprene and *n*-pentane have almost the same retention times. The oil was finally obtained by evaporating the solvent and isoprene. It is found from the chromatograms that, besides isoprene, only a small amount of light species had been produced in the extraction. In fact, as shown in **Table 3**, the three components recovered, oil, isoprene and solid residue, give a reasonable mass balance.

The mean molecular weights (measured by a vapor pressure osmometer, Hitachi model 115, using benzene solvent and benzil as a standard) of the oil produced with toluene, *n*-pentane and nitrogen are similar, ranging from 325–480. As shown in **Fig. 2**, the molecular weight distributions (measured by a gel permeation chromatograph, Shimadzu model LC4A, column of HSG-20-15-10 (polystyrene gel) with tetrahydrofuran as a mobile phase, at room temperature; detector at UV-254 nm) of the oils are not much different from each other.

Table 3 shows that supercritical extraction of a 9-mm cube sample with toluene at 653 K and 5.2 MPa produces about 57 wt% of oil and 40% solid residue in 5.5 h. Note that the supercritical extraction under these conditions is completed in 5.5 h (Fig. 1). Sulfur

Fig. 2. Molecular weight distributions of extracted oil, measured by gel permeation chromatography.

analysis (SO_2 produced by burning the sample in a stream of oxygen; absorbed in H_2O_2 aqueous solution; H_2SO_4 in the solution titrated with $\text{Ba}(\text{NO}_3)_2$ aqueous solution) shows that about half the sulfur contained in the rubber sample is extracted into the oil with toluene. Therefore, a solid residue of 40 g, for example, would consist of 29.4 g of carbon black and 3.3 g of zinc oxide, both contained in the rubber sample, and 0.9 g of sulfur and 6.4 g of char produced from the decomposition of rubber.

2.3 Scanning electron microscope photographs

Figure 3 shows an unextracted tire sample, with agglomerates of 1–8 μm rubber grains. **Figure 4** depicts an internal-section of the residual solid after extraction with nitrogen at 653 K and 5.2 MPa for 5.5 h, including a transient period of 1 h (according to Fig. 1, $W/W_0 = 0.60$). No individual rubber grains can be seen; most of the grains seem to have melted. Under the electron microscope the outside surfaces of the sample appear similar to the internal surfaces (Fig. 4).

Figure 5(a) shows an internal section of the residual solid after extraction with *n*-pentane at 653 K and 5.2 MPa for 5.5 h, including the 1-h transient period ($W/W_0 = 0.44$). **Figure 5(b)** is a picture of the outside surface of the same solid. Inside the solid there are cavities, suggesting vigorous decomposition of rubber material with *n*-pentane, while no cavities are seen on the outside surface. In fact, direct visual observation shows that the outside surface has a structure totally different from the inside. The exterior of the solid is covered with a hard shell, while the inside is porous.

Figure 6(a), which exhibits a large cavity, displays an internal section of the solid after being extracted with toluene for 2 h, including the transient period of 1 h, at plateau temperature 653 K and 5.2 MPa ($W/W_0 = 0.47$). After three more hours at 653 K and 5.2 MPa ($W/W_0 = 0.40$), another internal section of

Fig. 3. Electron microscope photograph of unextracted rubber sample.

Fig. 4. Electron microscope photograph of an internal section of residual solid after extraction with nitrogen at 653 K and 5.2 MPa for 5.5 h, including transient period of 1 h.

(a)

(b)

Fig. 5. Electron microscope photographs of residual solid after extraction with *n*-pentane at 653 K and 5.2 MPa for 5.5 h, including transient period of 1 h: (a) photo of an internal section; (b) photo of outside surface.

(a)

(b)

Fig. 6. Electron microscope photographs of internal section of residual solid after extraction with toluene under the conditions: (a) 653 K and 5.2 MPa for 2 h, including transient period of 1 h; (b) after an additional 3 h of extraction at 653 K and 5.2 MPa.

the solid is shown in Fig. 6(b). Note that Fig. 6(b) shows the solid residue when extraction is completed. Here the carbon-black framework is present all over the solid residue. The outside surface of the solid (not shown) appears similar to that in Fig. 5(b). The outside surface is hard, but this hard shell is thinner than that observed for *n*-pentane extraction.

2.4 Rate of extraction with *n*-pentane

The rate of decrease in solid weight during extraction with *n*-pentane is assumed to be of first order:

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

where W_{∞} is the weight at completion of the extraction, and k is the overall rate constant. Integration

during the constant-temperature period gives

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

where t_1 is the time when the autoclave reaches the plateau temperature, and W_1 is the weight of solid at time t_1 .

Figure 1 gives $W_{\infty}/W_0 = 0.41$, which establishes W_{∞} . Also, W vs. time and W_1 are known. The weight-decrease data during the constant-temperature period are shown for the two sizes of cubical samples in Figs. 7(a) and 7(b) as individual points. Knowing W_{∞} and W_1 , Eq. (2) suggests that a plot of $\ln(W - W_{\infty})$ vs. t should give straight lines whose slopes establish k . The rate constants so obtained are plotted against

(a)

(b)

Fig. 7. Weight decrease of rubber sample in sub- to supercritical extraction with *n*-pentane: (a) 3.5-mm cube sample at 653 K and 0.3–5.2 MPa; (b) 9-mm cube sample at 653 K and 0.7–5.2 MPa.

pressure in Fig. 8. These rate constants increase continuously with pressure of *n*-pentane, from subcritical to supercritical. Also, the constants for the 3.5-mm sample are larger than those for the 9-mm sample until the pressure reaches about 3 MPa. Above this pressure, k does not depend upon size in the range of 3.5 to 9 mm. The dependence of k on sample sizes at pressures lower than 3 MPa obviously shows the significance of internal mass transfer in the overall extraction process. Even in the range of pressures higher than 3 MPa, measurements with some more different-sized samples will be needed to separate possible mass transfer effect from k and to evaluate the intrinsic mechanism.

The solid curves in Figs. 7(a) and 7(b) are those calculated from Eq. (2) with the rate constants shown in Fig. 8. The experimental data, after attaining the plateau temperature, 653 K, seem to follow closely the first-order rate equation.

Fig. 8. Rate constant vs. pressure, in sub- to supercritical extraction with *n*-pentane.

Fig. 9. Effect of temperature on weight decrease, in supercritical extraction of 9-mm cube sample with *n*-pentane at 4 MPa.

2.5 Effect of temperature

Figure 9 shows the experimental weight-decrease data for supercritical extraction of 9-mm cube samples with *n*-pentane at a fixed pressure of 4 MPa and various plateau temperatures from 563–653 K. At 653 K the extraction is completed in about 9 h, while at 563 K the extraction is still going on at 90 h. Since the weight ratio W/W_0 for complete extraction is not known at the lower temperatures, rate constants are not determined. However, it is clear that the rate constant is a strong increasing function of temperature. Also, as shown in Table 4, the initial weight decrease during the transient (temperature-rise) period increases with temperature. At 653 K the weight decrease during the transient period (1 h) is 25%, while at 563 K (0.75 h) it is only 13%.

3. Discussion

Supercritical extraction under nitrogen produces oil with a molecular weight distribution and mean molecular weight similar to those of the oil extracted with *n*-pentane and toluene. However, the extraction rate is highest with toluene, followed by *n*-pentane and then nitrogen.

Electron microscope photos suggest that decomposition of rubber material takes place vigorously

Table 4. Weight decrease during transient period; supercritical extraction of 9-mm cube sample with *n*-pentane at pressure 4 MPa

Plateau temperature	Time, t_1 , required to reach plateau temperature		Weight decrease $1 - (W/W_0)$ at time = t_1
	K	s h	
563	2700	0.75	0.13
593	3000	0.83	0.17
623	3300	0.92	0.24
653	3600	1	0.25

with *n*-pentane and more violently with toluene. Perhaps this is due to the fact that rubber swells more in toluene than in *n*-pentane. When it swells more, it can be postulated that the rubber molecules become more disentangled and more easily decomposed into lighter species. Therefore, the solvent accelerates decomposition of rubber material; this effect will be more pronounced with the strong solvent, toluene, than with *n*-pentane.

It is presumed that lighter gaseous species produced by decomposition near the solid surface can easily go out, while there is a larger resistance for such species produced inside the solid to reach the outside surface. The gas stranded in the solid will have a pressure high enough to press against rubber material and make gas cavities: many such cavities are then produced throughout the solid, except in the vicinity of the outside surface. With the strong solvent, toluene, more decomposition takes place and more large cavities will be formed than with the weak solvent, *n*-pentane.

Once cavities are formed inside the solid, the lighter decomposition products can easily flow toward the outside surface. However, there are no cavities in the vicinity of the outside surface. The gas then has to flow through small extragrain spaces. While flowing in the cavity-less layer near the outside surface, the decomposition species may strike the grain surfaces and some will remain there. However, a strong solvent such as toluene dissolves the species and brings many of them to the outside surface of the solid and finally to the bulk fluid. The species remaining in the cavity-less layer will be carbonized and the outer layer becomes hard. In the case of *n*-pentane, more species will remain in the cavity-less layer because of its lower solubility; consequently, the hard shell becomes thicker than with toluene.

Nitrogen is not considered to be a solvent under normal conditions. However, when the pressure is high, nitrogen gas will penetrate into the rubber material and, to some extent, disentangle rubber molecules. Therefore, nitrogen also acts as a solvent at high pressure. This could explain why, as is

seen in Fig. 1, the weight-decrease rate becomes high as the nitrogen pressure increases. However, the decomposition proceeds slowly with nitrogen so that no cavities are made in the residual solid.

Table 3 shows that only a small amount of isoprene is produced in the extraction. This suggests that decomposition of rubber molecules occurs primarily by random scission of the molecules, and not by depolymerization. The mean molecular weight 325–480 of the oils suggests that the average molecules produced by the decomposition are polymers of a few isoprene monomers.

Conclusions

1) From the sub- to supercritical extraction data for used automotive tire (undertread) samples, the effectiveness of the solvents decreases in the order toluene to *n*-pentane to nitrogen. Nitrogen becomes more effective as the pressure increases.

2) The mean molecular weights of the oils extracted at 653 K and 5.2 MPa are about the same for all three solvents and are in the range 325–480. The molecular weight distributions of the oils are also similar. Supercritical extraction with toluene at temperature 653 K and pressure 5.2 MPa, for example, produces about 57 wt% oil and 40% solid residue when the extraction is completed.

3) Rates of extraction with *n*-pentane follow first-order behavior with respect to the weight of extractable material. First-order rate constants increase with increases in temperature or pressure.

4) A preliminary theory is presented for how extraction occurs in rubber.

Nomenclature

k	= first-order overall rate constant for weight decrease	[s ⁻¹]
r	= $-d(W/W_0)/dt$, weight decrease rate	[s ⁻¹]
t	= time	[s]
t_1	= time when autoclave reaches a prescribed plateau temperature	[s]
W	= solid weight	[kg]
W_0	= sample weight	[kg]
W_1	= solid weight when autoclave reaches a prescribed plateau temperature	[kg]
W_∞	= solid weight at completion of extraction	[kg]

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