

concentration and concentration flows through water-jacketed pipes at 90 °C. For safety, the unit, up to dehydration column, is swept by nitrogen. Thereafter, there is only a nitrogen blanket. In nitrogen flow, the oxygen content is kept lower than 3%. Nitrogen is washed with water, which is recycled to washing. Such a unit has been producing 1 t/h of hydroquinone and 1.5 t/h of pyrocatechol since 1973.

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Thermal Transfer Fluid: 1-Phenyl-1-tetrahydronaphthylethane

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Naphthalene was selectively hydrogenated to tetralin, followed by reaction with styrene to give 1-phenyl-1-tetrahydronaphthylethane in 87% yield. Efficient catalysts for the reaction were 90% sulfuric acid or solid acids possessing acid sites of $H_0 \leq -5.6$. Purified 1-phenyl-1-tetrahydronaphthylethane has favorable properties for a high boiling point thermal transfer fluid: boiling point, 342 °C; pour point, -37.5 °C; good thermal stability, etc. On severe heating, it decomposed to low fractions to some extent with little tendency to polymerization.

Introduction

Heat transfer fluids have been widely used for the exact control of processing temperatures in chemical plants. Among the various types of heat transfer liquids, hydrocarbon fluids are commonly used at high-temperature operations because of their low vapor pressure, noncorrosiveness, low toxicity, low production cost etc. There are two methods of heating: liquid phase and vapor phase. The former has better control and response characteristics than the latter. Certain mineral oils have been found to be adequate for liquid phase heating, but they are rather unstable at temperatures above 300 °C in closed systems. In order to maintain heat transfer fluids in the liquid state in nonpressurized heating units at high temperatures, their boiling point should be as high as possible. The low pour point is advantageous for plant operations in cold weather to avoid the necessity of steam tracing. Many synthetic fluids having better thermal stability than mineral oils have been developed. However, only two types, dibenzyl benzenes (Glass, 1964) and partially hydrogenated terphenyls (McDonald, 1972), are likely to satisfy the above-mentioned requirements.

In this article the synthetic method and the properties of a new high boiling point thermal transfer fluid, 1-phenyl-1-tetrahydronaphthylethane (PTE), are described. PTE is not a new compound, but little about it has been reported (Braun, 1921; Kusakov, 1961).

Experimental Section

Hydrogenation of Naphthalene. The hydrogenation of crude naphthalene (Nippon Steel Chemical Co.) was carried out in a 1-l. SUS 27 autoclave, using nickel-tungsten oxide (Nalco Chemical Co., NT-550) as a catalyst. Tetralin of the same amount with naphthalene was used as solvent. The agitation rate of the impeller was 1000 rpm. Such a high speed

could exclude the mass transfer effects on the hydrogenation reaction rate. The reaction mixture was distilled to give tetralin, which was then used for the reaction with styrene. In other cases the reaction mixture was directly subjected to the next reaction without distillation.

Reaction of Tetralin with Styrene. A weighed amount of catalyst and tetralin was placed in a four-necked round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, a reflux condenser, and a thermometer. Styrene was added to the mixture over a specific period with stirring at a constant temperature. The reaction mixture was separated from the catalyst. When sulfuric acid was used as catalyst, the reaction mixture was washed with 5% sodium hydroxide solution and then dried over anhydrous sodium carbonate. Distillation through a 20-cm Vigreux column gave PTE of 99.6% purity which consisted of 92.8% 1-phenyl-1-(5,6,7,8-tetrahydro-2-naphthyl)ethane and 6.8% 1-phenyl-1-(5,6,7,8-tetrahydro-1-naphthyl)ethane. IR: 1030, 910, 830, 770, 700. NMR: 1.55 (d, 3H), 1.75 (m, 2H), 2.65 (m, 2H), 3.92 (q, 1H), 6.75 (s, 3H), 7.04 (s, 5H). Found: C, 91.4; H, 8.6. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53.

Thermal Stability Test. There have been no authorized methods for testing the stability of thermal transfer fluids. In this work the following tentative method was adopted. A sample oil was placed in a 500-ml autoclave of SUS 27 and then sealed with nitrogen gas at a pressure of 3 kg/cm². The autoclave was heated at 375 °C with stirring at 500 rpm for a desired period. The pressure rise in the autoclave was recorded. After the autoclave was cooled to room temperature, the pressure was released and then the properties of the oil were measured by the following ASTM procedures: viscosity, D445; carbon residue, D189; flash point, D92.

Analysis. The reaction products were analyzed by GC supplemented by IR, NMR, and MS.

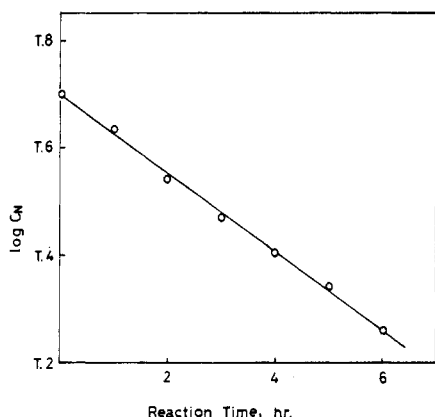


Figure 1. First-order plot of naphthalene hydrogenation.

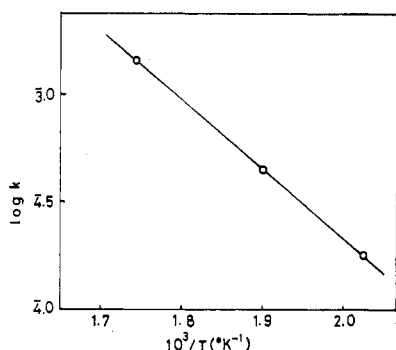
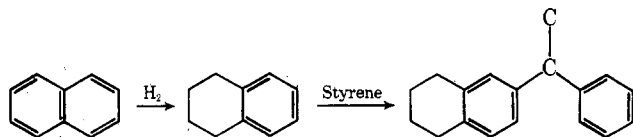


Figure 2. Arrhenius plot of naphthalene hydrogenation.

Determination of Solid Acidity. The amount and the strength of solid acids were determined by an *n*-butylamine titration method (Benesi, 1957).

Results and Discussion

Hydrogenation of Naphthalene. Styrene and commercial crude naphthalene from coal tar were chosen as starting materials for the PTE production, according to the reaction



The hydrogenation of naphthalene to tetralin is a well known process. Nickel catalysts are used commercially. Sulfur compounds in crude naphthalene, however, easily poison their catalytic activity. Metal sulfide catalysts have been reported to hydrogenate high sulfur naphthalene with an accompanying dehydrosulfurizing reaction. Quantitative data are still limited (Hogan, 1962; Eru, 1967; Sonoda, 1973).

In this work, hydrogenation was carried out in a batch-wise stirred reactor using nickel-tungsten oxide as a catalyst. A typical product distribution is shown in Table I. The selective hydrogenation to tetralin proceeded with little deca-stage hydrogenation and little subsequent cracking. Sulfur content could be reduced to below 10 ppm. The overall rate of the hydrogenation was found to be first order, as shown in Figure 1, by plotting the logarithm of naphthalene concentration against the reaction time. The first-order reaction rate was observed to be proportional to hydrogen pressure in the range 30–100 atm. Consequently, the reaction rate can be expressed by the formula

$$r = -\frac{dc_N}{dt} = KC_N P_{H_2}$$

Table I. Hydrogenation of Crude Naphthalene

Temperature, °C	300	
Pressure, kg/cm ²	90	
Time, h	6	
Composition, wt %	Crude naphthalene	Product
Xylenes	0	0.8
Dekaline	0	0.8
Tetralin	0	78.2
Naphthalene	99.1	20.0
Others	0.9	0.2
Sulfur content, ppm	445	10

Table II. Reaction of Tetralin and Styrene with Sulfuric Acid Catalyst

Temperature, °C	20	
Time, h	3	
Tetralin/styrene	3.0	
95% Sulfuric acid, wt %	3.7	
Conversion of styrene, %	99.8	
Yield based on styrene, %		
1-Phenyl-1-tetrahydro-2-naphthylethane	80.1	
1-Phenyl-1-tetrahydro-1-naphthylethane	5.8	
2,3-Bis(α -methylbenzyl)tetrahydro-naphthylethane	3.8	
Undistilled material	6.6	
Other	3.7	

An Arrhenius plot of the rate constant is shown in Figure 2, from which the apparent activation energy was calculated as 18 kcal/mol. The results described here are not sufficient for the determination of the reaction mechanism. It may be speculated, however, that the rate-controlling step involves the surface reaction in which the adsorption constants of the reactants are small, since it was unnecessary to incorporate the adsorption terms expressed in Hougen and Watson's type rate equation (Hougen, 1943) into the experimentally obtained rate equation.

Reaction of Tetralin with Styrene. It has been reported that alkylbenzenes react with styrene to afford diarylethanes in the presence of various acid catalysts (Spilker, 1932; Tsukervank, 1956; Sato, 1972; Socony Mobil Oil, 1961). In this study sulfuric acid of 85–95% concentration was found to be a satisfactory catalyst. In order to minimize the polymerization, styrene must be added dropwise to a mixture of stirred tetralin and sulfuric acid at a temperature below 40 °C. Thus, the selectivity to PTE based on converted styrene could be raised to 87%. Table II lists the results. No styrene dimers (Corson, 1954) were found in the product.

With respect to pollution caused from the waste catalyst, solid acids are preferable to sulfuric acid. Various solid acids were tested for the PTE preparation. Phosphoric acid on diatomaceous earth which is known to be a typical catalyst for the alkylation of benzene with olefins (Wesley, 1974) was practically inactive in PTE synthesis. Macroreticular sulfonated ion-exchanged resin also presented only 25% yield, though it has been reported to be highly active for the propylation of benzene and xylenes (Kapura, 1973; Morita, 1972). Figure 3 summarizes the results. A good correlation exists between the yield of PTE and the acid amount at $H_0 \leq -5.6$, with the exception of a rare earth cation-exchanged faujasite. Relatively low activity of the faujasite in spite of having a large acid amount may be attributed to its small pore size compared with a bulky PTE molecule. It has been reported that the catalytic activity is attributed to be acid centers at strength $H_0 \leq -3.0$ in the alkylation reaction of toluene with 1-butene (Morita, 1974). A patent (Gomi, 1975) has claimed the use of solid acids having appropriate acid amount at $H_0 = 0.8$ for the alkylation of tetralin with propylene, isobutylene, and other

Table III. Physical Properties of PTE

Density, 15/4 °C	1.035
Viscosity, cSt/100 °F	16.17
cSt/210 °F	2.90
Flash point, °C	182
Pour point, °C	-37.5
Boiling point, °C/mmHg	342/760
	199/12
	184/5
	167/0.6

Table IV. Change of Composition of PTE on Heating Test

Composition, %	Fresh	After heating
Benzene	0	0.6
Toluene	0	7.4
Ethylbenzene and xylenes	0	1.8
Tetralin	0	1.9
Methyltetralin	0	9.0
Naphthalene	0	1.3
Methylnaphthalene	0	4.4
PTE	90.5	44.2
1-Phenyl-1-naphthylethane	8.9	22.8
2-Benzyltetralin	0	2.5
1-Methyl-4 or 5-(α -methylbenzyl)indane	0	1.5
1-Ethyl-4 or 5-(α -methylbenzyl)benzocyclobutene	0	0.9
1-Phenyl-2-(tetrahydronaphthyl)ethane	0	1.0
Others	0.6	0.7

olefins. From Figure 3 it was obvious that the aralkylation of tetralin with styrene requires stronger acid sites than those required for common alkylation reactions.

Physical Properties. Typical physical properties of PTE of 99.6% purity are listed in Table III. PTE satisfies the desirable requirements for a thermal transfer fluid, i.e., high boiling point, low pour point, appropriate viscosity, and high flash point.

In practice, pure PTE is not essential. Mixtures of PTE and 1-phenyl-1-naphthylethane (Spilker, 1932), which were obtained by the reaction between styrene and the undistilled products of the hydrogenation reaction of naphthalene, are also useful. Mixtures containing a large ratio of 1-phenyl-1-naphthylethane, however, separate out crystalline 1-phenyl-1-naphthylethane on standing at low temperatures, though the properties of the mixtures do not differ much from those of pure PTE listed in Table III. The maximum allowable content of the compound was found to be 30 wt %.

Thermal Stability. When conventional hydrocarbon fluids are exposed to high temperature, thermal cracking occurs. While thermal cracking forms volatile products, it also produces heavier condensates. Volatile products lower the flash point of the liquid; on the other hand, heavier products lead to the formation of coke-like deposits. It is known that the shorter alkyl side chains combined to aromatic rings are more resistant to thermal cracking than the longer ones (Asselin, 1964). PTE, therefore, has a favorable structure, but it does suffer some thermal degradation on severe heating. The thermal stability test was carried out by heating the sample fluids in an autoclave at 375 °C. The viscosity changes, the flash point, and residual carbon and the pressure rise in the autoclave are indicated in Figure 4. PTE is compared with a typical mineral thermal transfer oil and two excellent commercial synthetic fluids, i.e., dibenzyl benzene and partially hydrogenated terphenyl. The pressure rise can be regarded as a

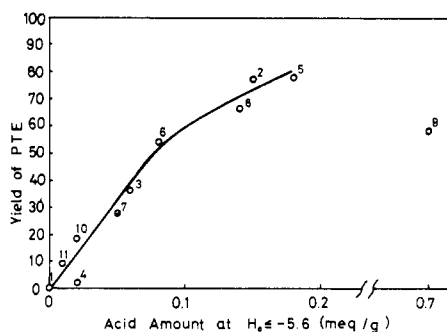
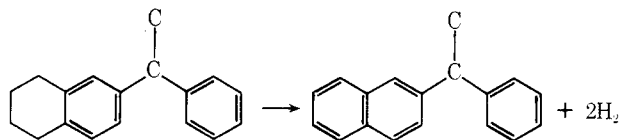
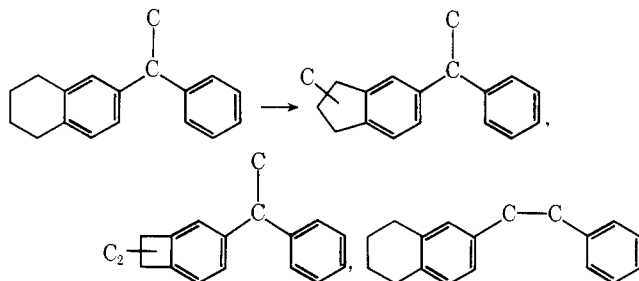


Figure 3. Relation between activity and acid amount (temperature, 150 °C; reaction time, 3 h; mole ratio of tetralin to styrene, 4.0): 1, bentonite, untreated; 2, bentonite, treated with 15% H₂SO₄ for 3 h; 3, bentonite, treated with 15% H₂SO₄ for 15 h; 4, montmorillonite, untreated; 5, montmorillonite, treated with 15% H₂SO₄ for 3 h; 6, commercial active clay a; 7, commercial active clay b; 8, silica-alumina; 9, RE-zeolite Y; 10, phosphoric acid-diatomaceous earth; 11, molybdena-alumina.

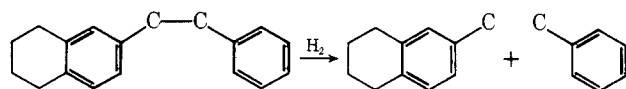
measure of the thermal cracking of the fluids to low-boiling fractions. The evolved gas from PTE consisted of hydrogen and lower molecular hydrocarbons (e.g., methane, 96.8%; ethane and ethylene, 2.1%; propane, 0.4%; propylene, 0.1%; C₄ ~ C₅, 0.6%). The liquid composition of PTE after heated for 300 h is given in Table IV. The data indicate that the main reaction of PTE on severe heating is the dehydrogenation of a saturated ring



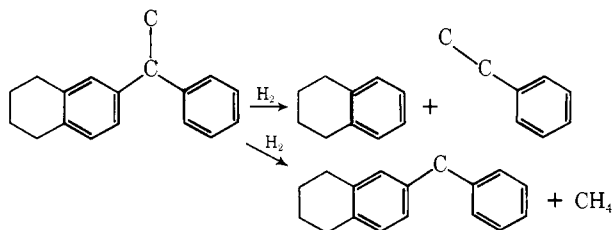
The isomerization reaction is also revealed to occur to some extent



Since 1,2-diphenyl-substituted ethanes are far more unstable than 1,1-diphenyl-substituted ones, the resulting 1-phenyl-2-tetrahydronaphthylethane may be easily hydrocracked to methyltetralin and toluene



The direct hydrocrackings of PTE are also shown to proceed to some degree



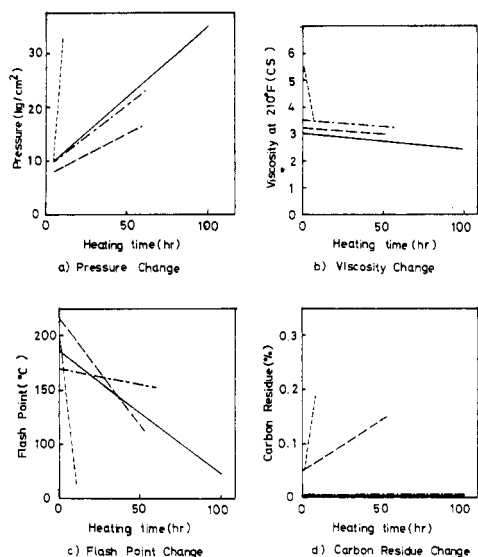


Figure 4. Thermal stability test: —, PTE; ---, dibenzylbenzene; - · - · -, partially hydrogenated terphenyl; · · · ·, mineral oil.

The rupture of a saturated ring is considered to occur to a lesser extent, because it would produce larger amounts of C₂ and C₃ hydrocarbons and 1-phenyl-1-alkylphenylethane than those observed. Nowak (1975) also has reported that the reaction rate of the saturated ring rupture is much less than the dehydrogenation and the isomerization in the thermal cracking of tetralin.

Figure 4d shows the change of carbon residues which are the measure of polymeric product contents in the fluids. Polymers formed through the degradation of fluids first darken the mass and from the dissolved state soon deposit on the heater and other surfaces of the system. The deposits are liable to cause serious trouble on the industrial operation of heating systems. Carbon residue of PTE hardly changed after

a 100-h heating test, in contrast to benzylbenzene. Moreover, the degree of darkening of PTE was less than that of partially hydrogenated terphenyl. Thus, PTE was indicated in this test to have little tendency toward polymerization.

In conclusion, PTE has thermal stability comparable to dibenzylbenzene and partially hydrogenated terphenyl. It shows promise of long life without much degradation below about 330 °C when used in air-free closed systems.

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