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Formation of dl-Limonene in Used Tire Vacuum Pyrolysis Oils

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Introduction

Tire recycling has become an important environmental issue recently due to the huge piles of tires that threaten the environment. There is about one worn tire produced per person per year in the developed countries (1).

Thermal decomposition of tire, a synthetic rubber material, enables the recovery of carbon black and liquid hydrocarbon oils. Both have potential economic values (1). Pyrolysis oils obtained under vacuum conditions contain a significant portion of a volatile, naphtha-like fraction with an octane number similar to petroleum naphtha (2). The benzene, toluene, and xylene (BTX) content of this naphtha fraction is also remarkably high. This naphtha fraction, in addition, contains approximately 15% limonene. Potential applications of vacuum pyrolysis oil (2) and carbon black (3) have been investigated. However, the process economics is greatly influenced by the quality of the oil and carbon black products (4).

This paper discusses limonene formation during used tire vacuum pyrolysis and its postulated reaction mechanism. The limonene separation method from pyrolysis oil, as well as its purification in laboratory scale, and structural characterization are discussed. Large-scale limonene separation and purification is under investigation.

Limonene: Usage, Value, and Market

Limonene is the chief constituent of citrus oil (over 60%) and is mainly obtained by expression from the fresh peel of grapefruit, lemon, and bitter and sweet orange at yields of 0.60%, 0.35%, 0.15%, and 0.30%, respectively. Limonene exists in two forms: d-limonene, the most naturally abundant, and dl-limonene (dipentene). Dipentene in addition is formed during the processing of sulfate liquor from kraft paper manufacture. Except for its optical ac-

tivity, dipentene has the same physical properties as d-limonene. Its normal boiling point is 175.5–176.5 °C. It has a density of 0.3402 and is insoluble in water but miscible with alcohol.

Limonene has an extremely fast growing wide industrial application. It is used in formulation of industrial solvents, resins, and adhesives and as a dispersing agent for pigment. It is also used as feedstock for the production of various kinds of terpenoid alcohol fragrances. *l*-Carvon, for example, is synthesized from limonene and is used in the manufacture of synthetic spearmint flavoring in toothpastes and mouthwashes (5). Originally, these alcohols were isolated from essential oils. During the past 20 years, development of terpene alcohol chemistry and its application in perfumery has increased considerably and has led to the manufacture of olfactively high value products. The solvency of limonene and its swelling and softening properties make it useful for rubber reclaiming in the processing of natural and synthetic rubbers. It is sometimes used as a diluent for pine oil in flotation applications (6).

The ever growing concern about the potential toxicity and environmental impact of conventional industrial cleaning solvents has been widely reported (7). This has stimulated interest in the use of limonene, a natural solvent, because of its pleasant nature, excellent solvency, rinseability, and high wetting, penetrating, and detergent properties. Limonene, a solvent and a fragrance, is also biodegradable and environmentally safe. It is not surprising that it has gained extension of its use into a wide range of applications including water-based degreasers, natural lemon-scented all-purpose cleaners, and lotion-like waterless hand cleaners. Limonene has been recently incorporated as the main ingredient of over 100 household cleaning agents and industrial hand cleaners due to its environmental safeness. Various chlorinated and fluorinated solvents, such as the chlorofluorocarbons (CFCs) used in electronic circuit board cleaner formulation (180 Mt/year worldwide), are now being partially replaced by

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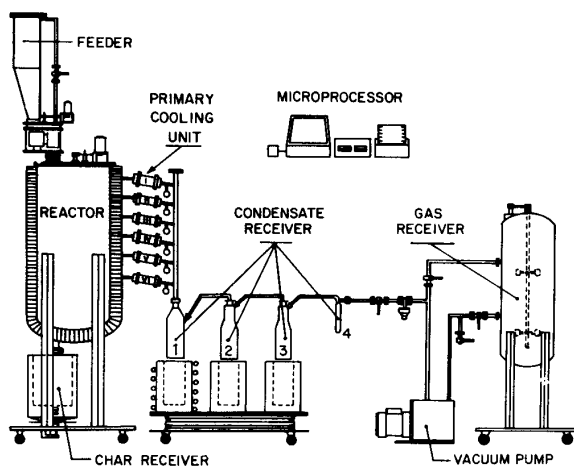


Figure 1. Schematic of the vacuum pyrolysis multiple hearth furnace.

limonene. All CFCs will be completely out of use before December 1999 (7, 8).

As a result, the demand for limonene has significantly increased over the last 2 years and prices are steadily rising. Limonene had a 50% growth demand over the 12 months to May 1989 (9). Worldwide demand for limonene in 1988 was ~24000 t/year (10). About 65% of the total limonene is used in the resin industries (10). Citrus oil has received an increased interest during the last few years but its supply is severely limited to the seasonal upswing. Citrus oil supply tightens and market price fluctuates as the citrus season ends or when unfavorable crop raising conditions occur. It has been reported that the demand for citrus oils and their derivatives is growing faster than its supply so that no real balance between supply and demand is expected in the near future (11). Limonene prices doubled from \$0.80/kg during 1987 to \$1.60/kg during 1988. By July 1989 its price was varying between \$2.40 and \$3.00/kg (5).

Experimental Section

The pyrolysis oil samples used in this investigation were produced from used tires in a multiple hearth vacuum pyrolysis process development unit (PDU). The reactor was a six-hearth furnace, 2 m in height and 0.7 m in diameter. The system operated in a semicontinuous feed mode using shredded cross-ply tires ($1/4$ - $1/2$ -in. Tyler sieves). The reactor maximum temperature and total pressure were 510 °C and 1 kPa, respectively. The feeding rate was 3.5 kg/h. The PDU shown in Figure 1 has been described in details elsewhere (2). The organic vapors were removed from the reactor chamber by a mechanical vacuum pump and condensed in a series of condensers (H-I-H-VI) installed in parallel at the reactor outlets corresponding to the six reactor hearths (runs C022 and C026). The noncondensed vapors from the primary condensing unit (PCU) were collected in a train of receivers (C-1-C-4), which served as a secondary condensing unit (SCU). The reactor hearth temperatures were stabilized at 226, 295, 366, 404, 450, and 510 °C from top to bottom, respectively. The process yielded 55% (by weight) oil, 25% carbon black, 9% steel, 5% fiber residues, and 6% gas during a typical run.

A pro rata mixture of the pyrolysis oils from H-I to H-VI and C-1 to C-4 was prepared and distilled under atmospheric pressure up to 204 °C to separate the naphtha fraction. A 1-g aliquot of the distillate was fractionated over 20 g of impregnated silica gel (10% AgNO₃, 60-200 mesh).

Table I. Major Compounds Identified in Naphtha Fractions and Recovered from Different Reactor Hearths (wt % in Naphtha)

compound	hearth I-VI (pro rata sample)	hearth ^a		
		II	III	VI
methylpentane	1.44	0.71	1.02	nd
dimethylpentane	1.04	1.12	0.92	1.26
benzene	2.54	0.86	1.01	2.30
2,4,4-trimethyl-1-pentane	1.43	0.64	nd	nd
dimethylcyclopentadiene	1.58	1.25	1.60	2.25
toluene	6.95	2.87	3.49	8.54
trimethylpentadiene	0.46	0.21	0.22	1.30
ethylhexadiene	0.83	0.98	1.22	0.76
4-vinyl-1-cyclohexene	1.66	nd	0.48	nd
3-methyl-1,4-hexadiene	0.41	nd	0.16	0.97
p-xylene	2.78	0.82	1.20	4.36
m-xylene	2.43	1.30	1.81	1.31
o-xylene	0.91	0.39	1.06	0.98
isopropylbenzene	0.97	nd	0.38	nd
dipentene	14.92	2.40	3.88	trace

^a nd, not detected.

The first fraction was eluted with 50 mL of *n*-pentane and followed by elution with 100 mL of 5% dichloromethane in *n*-pentane in 5-mL fractions. All fractions were analyzed by GC. Limonene was identified with a purity of over 80%. The limonene fraction was further purified by thin-layer chromatography, which resulted in 95% purity. The product was further analyzed on a Carl Zeiss 369414 polarimeter for its optical activity.

Gas chromatographic analysis was performed on a Varian 6000 gas chromatograph with a 30 m × 0.25 mm i.d. DB-5 (J&W) capillary column and FID detector. The GC oven temperature was held at 35 °C for 10 min and then increased to 100 °C at 2 °C min⁻¹ and to 290 °C at 30 °C min⁻¹.

A Nicolet 60 SX FTIR spectrometer coupled to a Varian 6000 gas chromatograph was also used to characterize the total naphtha fraction.

Results and Discussion

Gas chromatographic analysis of the pyrolysis oils obtained from the reactor hearths, H-I-H-VI, as well as a naphtha fraction from a pro rata oil, was performed. Unambiguous assignment of dipentene (*dl*-limonene, racemic form) was made by coinjection of an authentic sample of dipentene (from Aldrich) and by GC/FTIR analysis. Polarimetric analysis of the purified limonene sample also confirmed its racemic structure. Dipentene contributed 15% of the naphtha fraction, or 2.2% by weight of the as-received tires. Besides dipentene, a few other compounds, some of which were not reported before in the literature (12-16), were identified (Table I).

The naphtha yield represented 26.8% of the total pyrolysis oil. Its compositional analysis revealed a higher aromatic hydrocarbon content compared with the petroleum naphtha, thus reflecting its higher octane number. However, it suffered from high olefinic hydrocarbon content, which is not desirable since these olefins lead to the formation of gums. The naphtha has a gross calorific value of 43.7 MJ/kg, slightly lower than petroleum naphtha (46.5 MJ/kg) (17).

GC analysis of the pyrolysis oil from H-I (reactor top, lowest temperature zone) to H-VI (reactor bottom, highest temperature zone) revealed the presence of dipentene in H-II (295 °C) to H-V (450 °C) whereas only a trace amount was observed in H-I (225 °C) and H-VI (510 °C) oils. H-IV oil exhibited the highest dipentene content. Thus, a temperature range of 295-450 °C was found to be the most

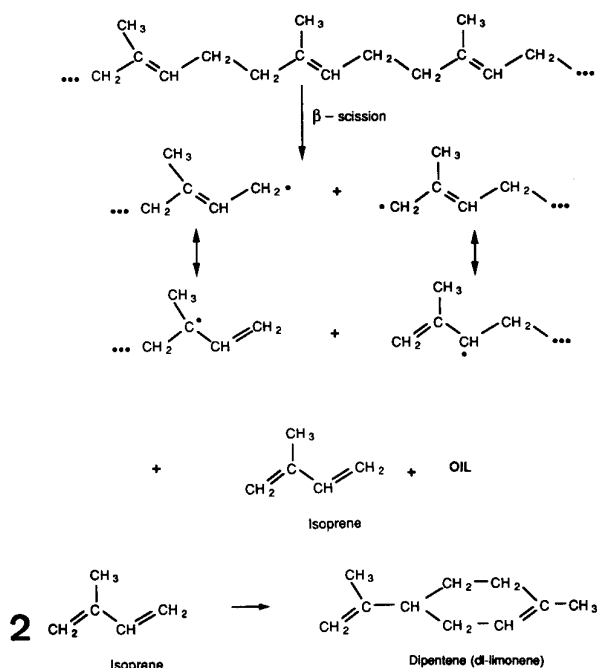


Figure 2. Postulated mechanism for the production of *d,l*-limonene during vacuum pyrolysis of rubber.

likely rubber degradation temperature range under vacuum for dipentene production. 4-Vinyl-1-cyclohexene (1.7%) was also identified in the naphtha fraction in a similar temperature range.

Tires are principally made of styrene and butadiene copolymer (SBR), polybutadiene, or a mixture of polybutadiene and polyisoprene. Thermal decomposition of natural rubber has been studied over the years under both atmospheric and subatmospheric pressure conditions and up to approximately 700 °C. During the late 1920s, Midgley and Henne (18) found that isoprene and dipentene were the dominating products of the destructive distillation of rubber. The degradation behavior of rubber is a function of the process conditions used, cross-linkage, and how rubber is cured. Most of the thermal degradation studies of rubbers have been made under inert atmospheric conditions. A recent investigation by Tamura and co-workers reported that diene rubber undergoes thermal random scission along the main chain in vacuo or in an inert gas, producing polythiyl radicals (19). The polymer radicals produced at temperatures below 250 °C will react by recombination, addition, and disproportionation reactions in the solid-liquid phase. Various gaseous primary fragments including isoprene and butadiene monomers are produced at temperatures typically between 250 and 450 °C.

As the reaction proceeds further, two isoprene or butadiene molecules formed in the initial stages will be rapidly converted to secondary products, 1-methyl-4-(1-methylethenyl)cyclohexene (dipentene) and 4-vinyl-1-cyclohexene, by means of a Diels-Alder reaction (Figure 2).

Dipentene and 4-vinyl-1-cyclohexene yields depend on the reaction temperature. Intermediate free radicals and dimers, dipentene for example, are also thermally unstable at higher temperature and reaction will proceed by recombination and further pyrolysis following dehydrogenation and reverse Diels-Alder reactions. Since we did not observe any significant amount of dipentene and 4-vinyl-1-cyclohexene in H-VI oil (Table I), it was therefore concluded that either dipentene formation ended below 450 °C (H-VI hearth) or it decomposed spontaneously after

formation at 510 °C (H-VI hearth).

Thermal reaction of 1,3-butadiene had been studied earlier at higher temperatures (550–750 °C) (20). 4-Vinyl-1-cyclohexene was the sole product below 600 °C. As the reaction temperature was raised, cyclohexene, cyclohexadiene, benzene, butene, propylene, ethylene, methane, and hydrogen were formed. C_6 cycloolefins are intermediate compounds. Their concentrations increased during the initial stage of the reaction, passed through maxima, and eventually were converted to the final aromatic products through reverse Diels-Alder reactions, dehydrogenation reactions, or both. Hydrogen and methane, which are thermally stable, increased as the reaction progressed.

An earlier report on pyrolysis of synthetic rubber at 350 °C under atmospheric pressure of nitrogen similarly showed dipentene as the major initial product, which was followed by disproportionation to the other derivatives such as methylisopropylbenzene under prolonged heating (21). In the same work, the authors observed that under certain conditions dipentene, the expected major product, was no longer a significant component. Carbon black, sulfur, and other metallic oxides tended to accelerate dipentene disproportionation reaction.

This could explain why dipentene has not been observed in tire pyrolysis oils obtained at temperatures above 500 °C, as described earlier in the literature. In fact, it is known that vacuum accelerates the removal of unstable gas and vapor molecules from the hot chamber and considerably reduces the occurrence of secondary reactions.

Large-scale separation of dipentene is presently under investigation. It is anticipated that the separation process will require at least two consecutive distillation steps followed by a purification step.

Conclusion

The presence of large amounts of dipentene and BTX chemicals in the light fraction of the used tire vacuum pyrolysis oils positively influences the economics and feasibility of the thermal decomposition process. High dipentene content of the oil was associated with the stepwise increase in the pyrolysis temperature from 225 to 450 °C during the pyrolysis process. Vacuum accelerated dipentene formation and prevented further degradation of the molecules at higher temperatures. Dipentene was analyzed, separated, and purified at laboratory scale. Further work is underway in a scaled-up separation system for dipentene recovery.

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