



## Review

## Liquefaction of waste tires by pyrolysis for oil and chemicals—A review



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## ABSTRACT

This article provides a critical review of past efforts over the last four decades in oil and liquids production from the pyrolysis of waste tires. Experimental lab-scale and pilot-scale results from the pyrolysis of scrap tires are included here. The various operating conditions under which pyrolysis of waste tires is carried out are reviewed. In addition to reactor conditions such as temperature and heating rates, other aspects of the tire pyrolysis such as catalyst type, catalyst preparation, and their effects on oil yields are also reviewed. Pyrolytic oil characteristics such as heating value, sulfur content and density are summarized. The various issues with production of oil from tire pyrolysis such as sulfur content, gaseous combustion emissions, naphtha composition are also discussed in the review. Various methods for the analysis of the pyrolytic oil composition and its refining to produce valuable products are evaluated. The review revealed that the pyrolytic oil could yield useful chemicals such as the aromatic benzene and limonene, in addition to fuel applications, depending on the type of waste tires pyrolyzed and the operating conditions of the pyrolysis process.

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## 1. Introduction

Waste tires are a significant part of the urban waste stream that is growing in quantity. It was estimated that the European Community generated an estimated 4.5 million tons of new tires in 2010 [1], with 289 million tires being replaced that year [1]. In the United States alone, approximately 500 million scrap tires were generated in 2007, with about 128 million used tires already currently stockpiled throughout the country [2]. In Australia, around 52.5 million equivalent passenger unit (EPU) tires reached their end of life (one EPU = 8 kg) in 2007–2008. Approximately 64% of these tires went to landfill, or were illegally dumped or stockpiled, while only 13% of them were recycled [3]. In 1998, the world production and sales of tires were estimated to have attained a new milestone by passing over the one billion mark, with 2007 estimates reported at 1.3 billion tires [4]. Since it is generally accepted that for every tire sold in the market another joins the waste stream, approximately 1.3 billion tires reach the end of their life cycle annually.

Waste tires resist degradation due to the vulcanization process during its production. The vulcanized rubber consists of long chain polymers (isoprene, butadiene, and styrene–butadiene) that are cross-linked with sulfur bonds and are further protected by antioxidants and antiozonants [5]. In landfills, rubber tires are not degraded easily, but tend to float to the top over time due to trapped gases, thus breaking landfill covers [6]. Combustion of tires produces toxic gases, which contain carcinogenic and mutagenic chemicals [6,7], so tire incineration requires expensive air emissions control systems.

The main constituents of a typical tire compound are natural rubber (NR), styrene butadiene rubber (SBR), polybutadiene and butyl rubber, with small quantities of organic and inorganic additives. Three examples of tire constituents as reported in the literature, spanning three decades, from the 1980s to the 2000s, are shown in Table 1. Since tires are composed of mainly long-chain hydrocarbons, reprocessing tires to obtain these hydrocarbons could provide an economical way to treat this form of waste. Recovering the valuable hydrocarbons from waste tires for energy and chemical feedstock would reduce dependency on fossil fuels, which would in turn help mitigate the threats of decreasing reserves of fossil fuels and climate change.

A technically feasible way to treat tires and recover valuable products is pyrolysis. Pyrolysis is a process in which organic materials are thermally decomposed into simpler constituent components when subjected to high heat, under an oxygen-free atmosphere [8]. Thus, pyrolysis of polymers is also known as destructive distillation. One of the earliest studies on the pyrolysis of rubber was done during the late 1920s, where Midgley and Henne found that isoprene and dipentene were the dominating products [9]. The production of these chemicals and other liquids, especially oils, from pyrolysis of rubber

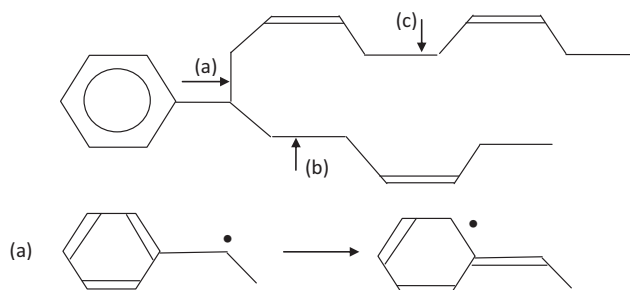


Fig. 1. Possible scission position for C–C bond in the SBR chain during pyrolysis and the resultant resonance aromatic structure for position (a).

has been studied over the years under many different conditions [10–98].

Many attempts have been made to investigate the thermal degradation mechanism of rubbers tires. Rubber polymers can be depolymerized through chain scission and side-group scission. Fig. 1 shows the possible areas of lysis in a styrene–butadiene rubber polymer. In most cases, chain scission was found to be more preferable during the pyrolysis of natural rubber [10], polybutadiene [11], and styrene–butadiene rubber [12]. Chen and Qian [10] found that  $\beta$ -scission was preferred in the pyrolysis of natural rubber because of the low bond dissociation energy, leaving the allylic radicals. Choi [12] showed that for styrene–butadiene rubber, scission was favored to occur at the position (a) than at (b) or (c), as shown in Fig. 1. This is due to the higher stability of the resonance forms due to the phenyl ring for the radical with the radical center on styrene, formed from the bond at (a). The scission at position (b) and (c) do not produce an aromatic compound with resonance (Fig. 1). In addition, decomposition reactions also occur concurrently with depolymerization during pyrolysis, to produce short chain hydrocarbons [10].

This review article critically examines the liquid products that had been produced by the pyrolysis of tires as reported in the literature over the last three decades. The various liquid products from the pyrolysis of waste tyres are discussed in terms of their respective production conditions (temperature, heating rate, gas flow rate, etc.), their composition and characteristics and the potential applications. An immediate application of the product liquid oils would be to use as a fuel. Thus pyrolytic oil fuel characteristics and emission performance are also discussed.

## 2. Experimental conditions for oil production

There are many variations in the pyrolysis conditions of waste tires, with different optimal conditions for the production of oils and liquids. The common parameters that researchers vary are pyrolysis temperature, heating rate, tire particle size, gas flow rate and pressure. These conditions are summarized in Table 2.

Table 1  
Tire constituents as reported in the literature.

Source	[10]	[7]	[86]			
Compound name and mass %	Natural rubber (SMR 5CV)	29.59	Styrene butadiene	46.78	SBR	43.5
	Styrene–butadiene rubber (SBR 1507)	29.59				
	Carbon black (ISAF N220)	29.59	Carbon black	45.59	Carbon black	32.6
	Stearic acid	0.59	Aromatic oil	1.74	Extender oil	21.7
	Zinc oxide	2.96	Zinc oxide	1.40	ZnO and sulfur	2.2
	Phenolic resin	2.37	Stearic acid	0.94		
	Aromatic oil	2.37	Antioxidant 6C	1.40		
	IPPD ( <i>n</i> -isopropyl- <i>n</i> '-phenyl- <i>p</i> -phenyldiamine)	0.89				
	Sulfur	0.89	Sulfur	1.17		
	CBS ( <i>n</i> -cyclohexyl-2-benzothiazol-sulfenamide),	0.89	Accelerator CZ	0.75		
	H-7 (hexamethylenetetramine)	0.18				
	PVI ( <i>n</i> -cyclohexylthio-phthalimide)	0.12	Wax	0.23		

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