Supercritical Toluene Extraction and Pyrolysis of Lignite - Tyre Mixtures

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INTRODUCTION

Tyres are made of more than 100 different substances. The main components are rubber (ca. 50 wt%), fillers like carbon black or silica gel (25 wt%), steel (10 wt %), sulfur (1 wt %), zinc oxide (1 wt%) and many other additives like processing oil, plasticizer or vulcanization accelerators[1]. The disposal of scrap tyres is a growing environmental problem, especially for industrial countries. The pyrolysis and extraction have been applied over the years to carboneous materials like coal or wood. Tyres contain polymeric aromatic structures that are similar to coal. Hence, the developed techniques used in coal utilization should be feasible to the pyrolytic destruction of waste tyres. Therefore, there has been an increased interest in the co-processing of waste tyre with coal. The solvent at its supercritical conditions acts as a medium to aid in the transport of hydrogen, as a heat transfer medium, as an additional reactant along with the coal, as a coal dissolution medium and as a medium to transport coal liquefaction products away from the coal matrix [2]. The presence of tire has a synergistic effect on coal conversion. The overall conversion of coal with tires by coliquefaction is greater than the sum of the individual conversion of coal and tires when they are liquefied solely [3,4]. The synergistic effect of the tire could be due to the presence of polyaromatic hydrocarbons produced during tire liquefaction and the tire oil may act as a hydrogen shuttle for coal liquefaction [5]. Another beneficial effect of the tire could also be due to interactions between coal and tire free radicals produced during the liquefaction process.

MATERIALS AND METHODS

A turkish lignite from west Anatolia and scrap tyre were mixed well in amount of 33 wt %, 50 wt % and 67 wt %. These weight percentages of scrap tyre in the mixtures were equal to lignite/scrap tyre ratios of 2:1, 1:1, and 1:2, respectively. The mixtures were pyrolysed at 400, 500, 600 and 700 ^{o}C and also subjected to the supercritical toluene extraction at the temperatures of 400, 450 and 500 ^{o}C. The effect of the experimental conditions on tar, gas, residual coke and water yield was determined. The variation of the yields and the effect of synergism on copyrolysis process was also investigated for both experimental runs.

RESULTS

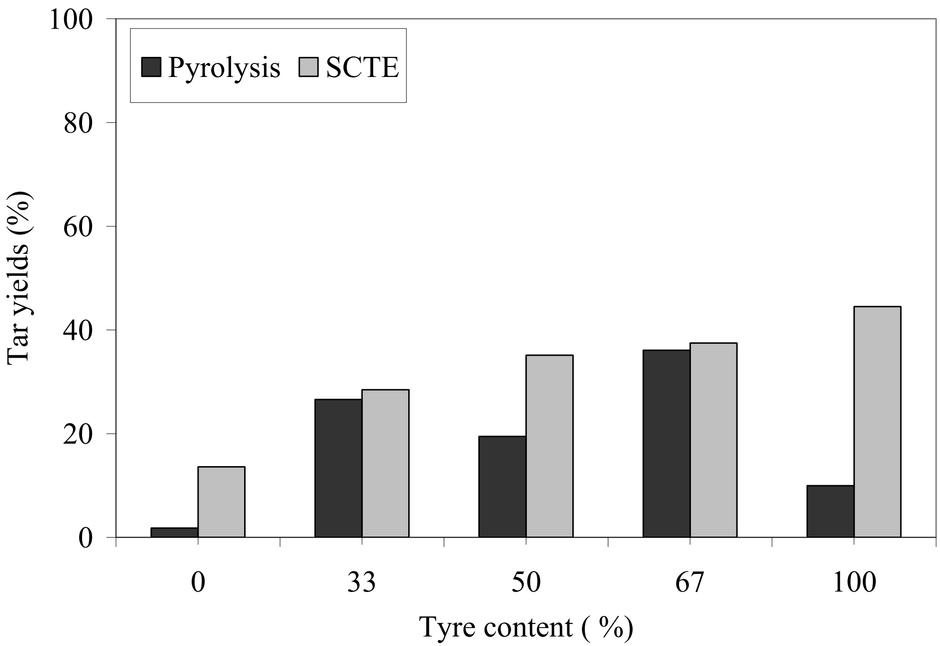

Figure 1. Effect of tyre content of the mixture on the tar yields obtained by pyrolysis and supercritical toluene extraction at 500 ^{o}C.

As can be seen in Figure 1, an increase in the scrap tyre content of the mixture leads to an increase in tar yields at 500 ^{o}C during the supercritical toluene extraction. Actually, maximum tar yields are obtained in the presence of 67 % tyre in both pyrolysis and supercritical toluene extraction. Supercritical toluene extraction seems to be more effective method to convert lignite and tyre mixtures to valuable products. In order to support this observation, the synergism is also considered during this study. Synergism is the event that two or more agents acting together having a larger effect than each one of them acting separately

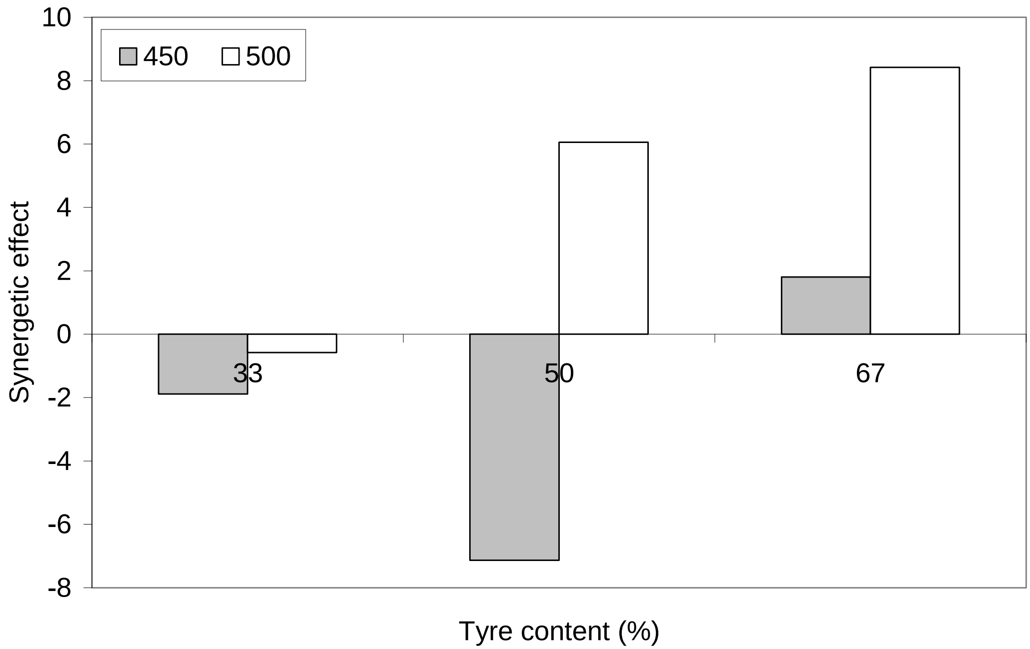

Figure 2. Effect of synergism on the tyre content of mixture for the tars recovered by supercritical toluene extraction.

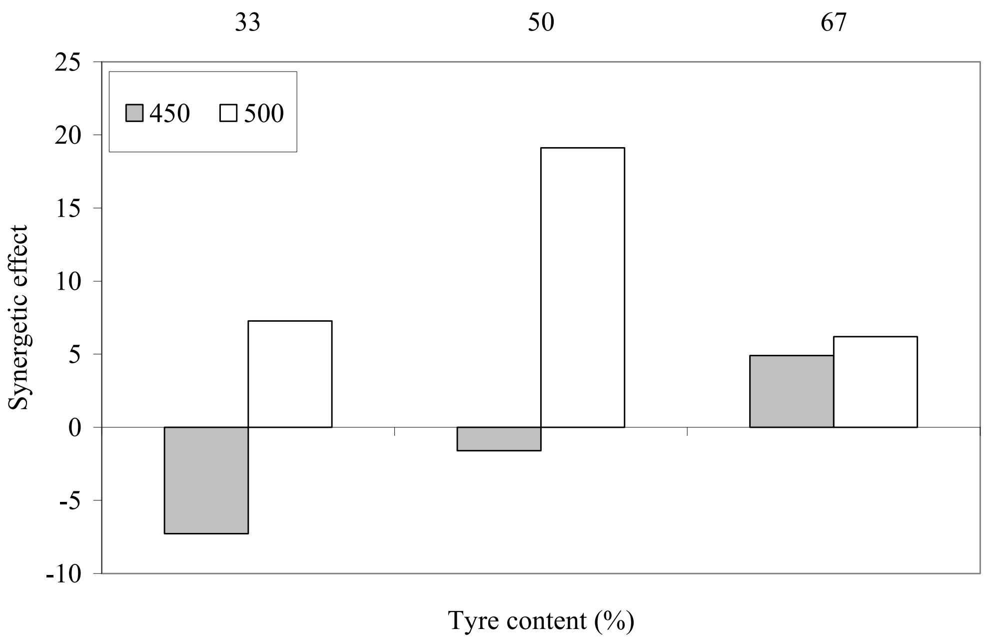

Figure 3. Effect of synergism on the tyre content of mixture for gas evolution recovered by supercritical toluene extraction.

Influence of synergism on the tar and gas evolution is given in Figure 2 and Figure 3 respectively. An increase in tyre content in the mixture at 500 ^{o}C leads to an increasing synergism between lignite and tyre for the tar. Synergetic effect on the tyre content is clearer on the gas evolution at the tyre content of % 50.
The reason of this might be related to the capping of the free radicals generated from coals by volatile substances evolved from tyre at higher temperatures and this inhibits hydrogen transfer reactions and, consequently, the generation of tar is increased as also shown by Vivero et al [6].

Temperature has a vital role in the degradation of tyre-like polymeric materials. From the mechanistic point of view, de-polymerization results from the scissions or cleavages of some weak linkages having energy less than 58 kcal mol-1, which result in the formation of free radicals. The radicals generated as a result of the scissions need to be stabilized by hydrogen to obtain volatiles. This is achieved by hydrogen released from the tyre. Thus, gas evolution is increased under the conditions explained above.

CONCLUSION

When the tar yields obtained by pyrolysis and supercritical toluene extraction compared, it can be obviously seen that the enhanced amount of tar is produced during supercritical extraction. To obtain valuable chemicals from the copyrolysis procedure, improved tar and gas yields are needed. This can be achieved by adding tyre to the lignite at 500 ^{o}C

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