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Improvement of Solid Product Quality in Pyrolysis of Tyre Derived Fuels (TDF)

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Waste tyres do not decompose easily in the nature and cause to many environmental problems. Although, 24 million tyres / y are produced and 8.5 million (180.000 t) of these amount become waste in Turkey, these waste tyres are not evaluated properly. Indeed, waste tyres can be used as a new source of energy and raw material through some thermal processes. One of the thermal processes is pyrolysis that waste tyres can be converted into gas, oil and solid product. For instance, solid product can be used as carbon black with some quality improvements especially removal of ash and sulphur.
In this study, it was focused on the improvement of solid product quality in pyrolysis of TDF. For this aim, TDF sample consists of different waste tyre types (SBR-Styrene-butadiene Rubber, CBR-Cis Polybutadiene Rubber) was pyrolysed by using a fixed bed reactor, at 400 $^{\circ}$C with 5 $^{\circ}$C/min heating rate. Sulphur and ash content of TDF and solid product samples were determined and compared with commercial carbon black values. It was seen that sulphur and ash contents of samples were higher than commercial carbon black. Therefore, solid product was treated with HCl and HNO_3 for the ash removing. And also, the effect of ultrasound on the photocatalytic oxidation (Sonophotocatalytic oxidation) of sulphur particles catalyzed by titanium dioxide was studied. As a conclusion, the improvement studies had a positive effect to decrease ash and sulphur content of solid product.

1. Introduction

Tyre rubber is a mixture of different elastomers such as natural rubber (NB), butadiene rubber (BR) and styrene butadiene rubber (SBR) plus other additives like carbon black, sulphur and zinc oxide. The disposal of waste tyre represents a major environmental issue throughout the world, since the same properties that make them desirable as tyres, most notably durability, also make their disposal and reprocessing difficult, they are almost immune to biological degradation (Mui et al., 2010).
Nowadays, end of life tyre, in addition to being abundant are position a worthless waste. They cause environmental pollution, influence natural balance and human health in negative anywise. One of the most effective way to solve the problem; waste tires were process again and used for different application in the industry. Over the last few years most commercial tyre recycling processes have focused on the use of ground tyre rubber

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in different applications including as an additive in playground surfaces, in rubber roofs, in drainage systems and in floor mats. A major market for scrap tyres is their utilization as solid fuels, especially in cement kilns (Roy et al., 1999).
24 million tyres are produced and 8.5 million (180.000 ton) tyres become waste tyres in Turkey yearly and evaluation of these waste tyres is very limited. In connection with the management of these wastes, the pyrolysis method that takes place in the section of applicable recovery methods for waste tyres of "Regulation For Control Of The Tyres Which Have Completed Their Life-Cycles (TCL)" that published on the Official Gazette of 25 November 2006, number 26357.
In a pyrolysis process as different from combustion, the solid partially decomposes and produces gaseous, liquid and solid residuals as pyrolysis products and solid product is utilized as carbon black. In Turkey, the eight five-year development plan that published from Prime Ministry State Planning Organization is about carbon black and synthetic rubber. According to this report, import of the carbon black increase from the other countries because of the low prices competition (SPO, 2001).
To convert waste tyres into char, a pyrolysis process is usually carried out at typically 400^{o}C to break down the cross linkage between carbon atoms. The resultant char characteristics are greatly influenced by the degree of burn off, which is often a function of temperature, holding time, particle size and heating rate.
Consist of solid products high ash and high sulphur are unsuitable for efficient use as a commercial carbon black. For instance, this study focuses on an understanding of the recovery of pyrolysis products and the removal of sulphur from TDF during pyrolysis.

2. Experimental

2.1. Materials

Waste tyres used in pyrolysis experiments were supplied from a tyre recycling plant and they formed into TDF. Pyrolysis experiments were carried out under atmospheric pressure at 400 °C in a fixed bed stainless steel reactor. In experiments, the reactor temperature was increased by heating rate of 5 °C/min up to the 400 ^{o}C and hold for 1 h at this temperature. The solid product was collected from the reactor and sonicated to decrease particle size. The results of the proximate and ultimate analysis of solid product and sulphur and ash value of commercial carbon black samples (HAF N330, HAF N550, Printex U) are compared in Table 1.

2.2. Methods

0.5 g of solid product were mixed 10 ml of concentrated acid (HCl, HNO_3 and 50 % mixtures of HCl and HNO_3) solutions. Sample solutions were digested in microwave oven (CEM MARS 5, 400W, 175°C, 6 min). After this period the mixture was separated by filtration. The insoluble fraction was washed, dried, weighed and the ash and sulphur content of this fraction were determined according to ASTM D-3174 and ASTM D-1619, respectively. Both demineralization and desulphurization of solid product were carried out by acid digestion.
The effect of ultrasound on the photocatalytic oxidation of sulphur particles catalyzed by titanium dioxide was studied. The batch reactor used in this study is shown in Figure

1 The components of batch reactor are a glass cell equipped with an ultraviolet tube, an ultrasonic horn (Titanium rod, 13 mm diameter) and an air inlet.

Table 1 Proximate and ultimate analyses results of solid product and commercial carbon black samples

	Solid Product	*HAF N330*	*FEF N550*	*Printex U (Degussa)*
Proximate analysis (%)				
Moisture	1.25	1.94	0.03	1.33
Ash	12.14	0.49	0.64	1.07
Volatile matter	15.65	10.79	11.76	17.22
Fixed carbon	70.92	86.78	87.57	80.38
Ultimate analysis (%)				
C	84.39	76.93	85.86	88.47
H	0.59	0.41	0.14	0.15
O[a]	10.72	18.99	3.35	1.05
N	2.59	3.17	10.65	10.33
S	1.71	0.5	-	-
GCV[b], MJ kg^{-1}	32.62	32.62	33.62	32.31

[a] *Calculated from difference*
[b] *Gross calorific value*

Typical experiments using the batch reactor were carried out by illuminating 800 ml of suspension in water, containing 1g titanium dioxide and 1 g sample that has elemental sulphur, between 0-1 g. Air was bubbled continuously inside the reactor in order to maintain the solution saturated with oxygen and to keep the TiO_2 and sulphur particles in suspension, which was visually confirmed. The light source used was 60Hz black tube lamp. The black bulbs (UVP Pan Ray Lamp, UK) emitted radiation 365 nm. The reactor was sonicated using an ultrasonic processor SONICS VCX 500 watts of 20 kHz that allows the control of ultrasound power. The process was completed after 1 h and then the mixture was separated by filtration. The insoluble fraction was washed, dried, weighted and sulphur content of samples was determined according to ASTM D-1619.

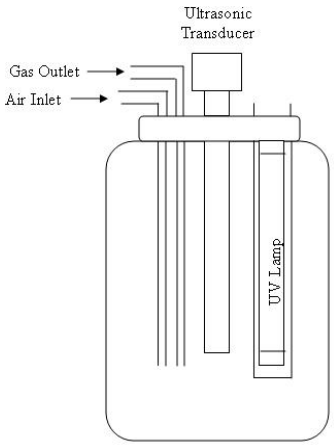

Figure 1: Experimental set up for the sonophotocatalytic oxidation

3. Results and Discussion

Results of solid product demineralization and desulphurization with acid are shown in Figure 2 and 3 as a function of acid type. The effects of treatment on the ash removal of solid product samples are shown in Figure 2, 12.14 % of mineral matter content of sample was removed by extraction with HCl (48.82 %) and HNO_3 (45.95 %). The results indicate that leaching with mixture of HCl and HNO_3 resulted in the highest degree of demineralization (60.52 %) and desulphurization (95.27 %). HCl was found to be effective than HNO_3 in demineralization process. But, it was not meet an expectation that was the aim of study to reach the HAF N330, FEF N550 and Printex U commercial carbon black ash values. Unlike the ash removal, sulphur content decreased rapidly. It was seen that acid digestion of solid product for the sulphur removal was enough to reach HAF N330 commercial carbon black sulphur value of 0.5 % but not enough to zero as FEF N550 and Printex U.

As shown as Figure 3, HNO_3 and HCl+HNO_3 treatments of sulphur particles have very effective removal (93.57 % and 95.27 % respectively). Sonophotocatalytic oxidation also has good removal (84.67 %). Although, treatment with only HCl didn't have removal efficiency (75.35 %) as high as the others, it provided required sulphur content when compared with HAF N330.

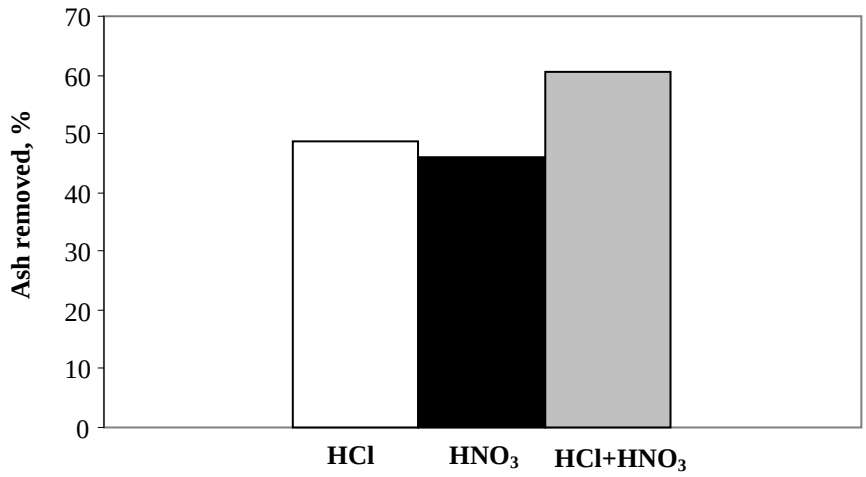

Figure 2: Results of demineralization of solid product by acid treatment

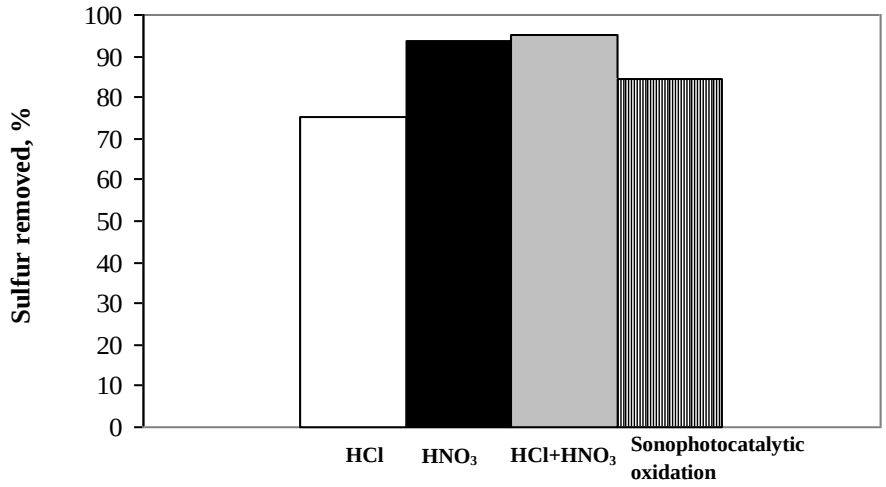

Figure 3: Results of desulphurization of solid product by acid treatment

4. Conclusion

It can be concluded that using HCl and HNO_3 mixture, a significant amount of mineral matter can be removed. The use of HCl and HNO_3 mixture resulted considerable sulphur reduction in solid product to reach the HAF N330 commercial carbon black

value. The simultaneous uses of TiO_2 photocatalysis and ultrasound have a positive effect on the oxidation reaction rate of sulphur particles. This observation is explained by the formation of fused particles between sulphur and titanium dioxide induced by the cavitation process. It seems that ultrasound combined with UV irradiation exhibits a synergistic effect, under the described experimental conditions.

Acknowledgements

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References

SPO, 2001, Rubber Product Specialism Commission Report, Carbon Black and Synthetic Rubber, Sub-commission Report, Eight Five-Year Development Plan, SPO: 2809-ÖİK 612, Ankara, Turkey.

Mui E.L., Cheung W.H., and McKay G., 2010, Tyre char preparation from waste tyre rubber for dye removal from effluents, Journal of Hazardous Materials 175, 151-158.

Roy C., Chaala A. and Damstadt H., 1999, The vacuum pyrolysis of used tyres; End-uses for oil and carbon black products, Journal of Analytical and Applied Pyrolysis 51, 201-22.