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Atık Lastik ve Haşhaş Kapsülü Küspesi Pirolizi: MgO-C Refrakterlerde Farklı Bağlayıcı Çeşitlerinin Araştırılması

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Anahtar kelimeler
Piroliz; Geri dönüşüm; Atık lastik; Haşhaş kapsül küspesi; MgO-C; Bağlayıcı

Öz

Bu çalışmada, MgO-C refrakterler için bağlayıcı elde etmek için iki farklı atık malzeme kullanılmıştır. Bunlardan biri sentetik atık olan atık lastik, diğeri ise biyokütle olan haşhaş kapsül küspesidir. Katı atıkların sıvı ürünlere dönüştürülmesi için uygun bir yol olan piroliz, bu atıkların sıvı bağlayıcılara dönüştürülmesi için uygulanmıştır. Bu pirolitik sıvıların gaz kromatografisi-kütle spektrometresi (GC-MS) analizleri incelenmiştir. Refrakterler, pirolitik sıvıları bağlayıcı olarak kullanarak üretilmiştir. Açık gözeneklilik değerleri, yoğunluklar gibi fiziksel özellikler ve Soğuk Basma Mukavemeti (SBM) gibi mekanik özellikler incelenmiştir. MgO-C refrakterlerin mikroyapı ve kırılma yüzeyleri, Taramalı Elektron Mikroskobu (SEM) ile tanımlanmıştır. Deneysel çalışmalar, fenolik bileşikler içeren bağlayıcıların kullanılmasıyla üretilen refrakterlerin daha yüksek yoğunluk ve mukavemete sahip olduğunu göstermiştir. Ayrıca, refrakterlerin mukavemeti gözeneklilik miktarından ters orantılı olarak etkilenmiştir. Çalışmanın sonuçlarına göre, atık biyokütle haşhaş kapsül küspesi pirolizi ile üretilen bağlayıcı, kimyasal bileşiminde fenolik bileşikler içermekte ve MgO-C refrakterinde atık lastikten üretilen bağlayıcıdan daha iyi mekanik özelliklere neden olmaktadır.

Pyrolysis Of Waste Tire and Poppy Capsule Pulp: Investigation Of Different Types Of Binders for MgO-C Refractories

Keywords
Pyrolysis; Recycling; Waste Tire; Poppy Capsule Pulp; MgO-C; Binder

Abstract

In the present study, two different waste materials were used to obtain binders for MgO-C refractories. One of them was waste tire which is a synthetic waste and the other one was poppy capsule pulp which is a biomass. Pyrolysis that is a suitable way for conversion of solid wastes into liquid products was applied for the conversion of those wastes into liquid binders. Gas chromatography–mass spectrometry (GC-MS) analyses of those pyrolytic liquids were examined. The refractories were produced by using the pyrolytic liquids as binders. The physical properties such as open porosities, densities, and mechanical properties such as Cold Crushing Strength (CCS) were investigated. The microstructure and fracture surfaces of MgO-C refractories were characterized by the Scanning Electron Microscopy (SEM). Experimental studies showed that refractories produced by the use of binders containing phenolic compounds had a higher density and strength. And also, strength of refractories was inversely influenced by the amount of porosities. According to the results of the study, the binder produced by pyrolysis of waste biomass poppy capsule pulp contained phenolic compounds in its chemical composition and caused better mechanical properties in MgO-C refractory than the binder produced from waste tire.

1. Introduction

Poppy Capsule Pulp is the main waste of Afyon Alkoloid Factory, Turkey which has been working for 30 years and accumulating the waste in the plant area. Today, according to the data taken from Afyon Alkoloid Factory, approximately 200,000 tons of Poppy Capsule Pulp are on the storage area of the Plant. Similarly, in 2010, the EU27 plus Turkey produced around 4.5 million tonnes of tires. It is assessed that more than 3.2 million tonnes of waste tires are discarded annually (Martinez et al. 2013). Due to increasing environmental and economic problems, those wastes are considered to be recycled or regained. Pyrolysis is a thermo-chemical conversion method occurring in the absence of oxygen to convert biomass and waste tires into valuable solid, liquid and gas products. Higher molecular weight compounds are broken to form lower molecular weight short chain molecules. The condensable liquid hydrocarbon mixture is known as pyrolytic oil.

There are many studies on pyrolytic conversion of different biomasses such as corn stalk (Cai et al. 2016), sesame stalk (Pütün et al. 2004), sugar cane bagasse (Erlich et al. 2005), cotton-seed cake (Pütün et al. 2006), pomegranate seeds (Uçar and Karagöz 2009), tamarind seed (Morales 2014), and Mahua seed (Shadangi and Mohanty 2014) into liquid fuels. However, for the first time in this study, pyrolytic oil produced from a biomass was utilized as a binder for refractory production. Also, a number of studies have been conducted to investigate the pyrolysis of waste tyres and how waste tyres pyrolysis may be optimized to produce pyrolytic liquids with high yield and high calorific value (Kumaravel et al. 2016 and Hooshmand et al. 2014). In the current study, different types of binders that were obtained from pyrolysis of waste tire and poppy capsule pulp were investigated for MgO-C refractories.

Magnesia-carbon bricks are well-established refractory products with particular properties for applications in converters, electric arc furnaces, and steel ladles (Int Kyn. 1). It is generally constituted of mixing, drying, pressing, and curing. During mixing, the powders of raw materials are coated by a layer of liquid phenolic resin. The binder of the shaped refractories is transformed into a solid state through the curing process (usually below 300 °C) (Zhang et al. 2018).

The binder that is blended in the mix before pressing maintains a specific strength for handling the ceramic body. This binder is removed while firing and ceramic inter linkages are formed mainly by solid state reactions at high temperatures. As long as the application temperature of these bricks does not exceed the firing temperature, there will be no change in these linkages. This is completely different in MgO-C-bricks. The role of the binder is of greater importance for those refractories, and it has a significant impact on the refractory properties and subsequently on the performance of the brick in service:

1. The binder works as a glue and gives green-strength to the brick.

2. After curing and hardening (duroplastic binders) or solidification (thermoplastic binders), it provides the as-delivered strength, necessary for handling.

3. The binder changes into carbon, and the organic bond is replaced by a carbon bond at high temperatures and under reducing atmospheres. After being transformed into carbon due to the temperatures in the steelmaking process, it works either as a bonding agent or a non-wetting agent to prevent slags from penetrating the brick (Int Kyn. 1).

Phenolic resins combine good workability and an acceptable environmental impact with good mechanical and chemical properties of those bricks. However, they are petroleum derived synthetic polymers, and so it is important to find green alternatives for these chemicals. In the present study, phenolic resin, which is a commonly used binder for MgO-C refractories, and two different kinds of pyrolytic liquids originated from two different waste materials were used as binders in MgO-C refractories comparatively.

2. Materials and Methods

Waste materials used for pyrolysis were waste tire and poppy capsule pulp that is a biomass discarded from alkaloid industry. Pyrolytic liquids were obtained by pyrolysis of waste materials in a fixed bed reactor at 500 °C temperature, 15 °C/min heating rate, and 0.5 lt/min N_2 flow rate parameters. Before using in refractory composition, the waste tire derived pyrolytic liquid was subjected to an acidic desulfurization because of its high sulphur content arising from sulphur addition during tire production. Acidic extraction with 10% of H_2SO_4 was applied. The kinematic viscosity measurements of liquids were done at 20 °C with a rotational viscosimeter (Fungilab, Smart series). The density values of liquids were measured at 20 °C according to the TS EN ISO 12185 method. The chemical components of the liquids were determined by GC-MS analyses (Agilent HP-5MS).

Prescriptions of MgO-C refractories (Table 1) were weighed with 2% Novalac, 0.02 % Hegzamin, 1% Antioxidant additions, and then blended. Refractory resin in L1, waste tire pyrolytic liquid in L2, and poppy capsule pulp pyrolytic liquid in L3 were used as binders. Graphite was used as a carbon source for those MgO-C refractories.

Table 1. Prescriptions of MgO-C refractory materials

Composition	1-4 mm MgO (%)	0-1 mm MgO (%)	< 63 µm MgO (%)	0-1 mm Flake Graphite (%)	Phenolic Resin (%)	Waste Tires Pyrolytic Liquid	Poppy Capsule Pulp Pyrolytic
L1	50	30	10	10	2	0	0
L2	50	30	10	10	0	2	0
L3	50	30	10	10	0	0	2

50mm×50mm×50mm (width×length×height) square prisms were shaped by applying 100 MPa pressure for each refractory materials. Those shaped materials were tempered in Nabertherm N11/R model ash furnace at 250 °C for 3 hours with 5 °C/min heating rate. Open porosities and densities of samples were determined by Archimedes principles. Cold crushing strength test was applied to each material by using a Liya compression testing machine.

Characterization of microstructures were performed by SEM-Mapping analysis with backscattered electron images at 1000x magnification. Also, elemental analyses of those refractories were examined by Energy Dispersive X-Ray Analysis (EDX) analysis. Fracture surfaces of samples were characterized by SEM with secondary electron images at 1000x magnification.

3. Results and Discussion

3.1 Properties of Waste Tire Pyrolytic Liquid, Poppy Capsule Pulp Pyrolytic Liquid, and Phenolic Resin

The amount of sulphur in waste tire pyrolytic liquid was reduced from 1.56% wt. to 1.08 %wt. after two times of acidic extraction. Poppy capsule pulp pyrolytic liquid was used directly after pyrolysis without acidic extraction because it did not contain any sulphur containing compounds. The physical properties of phenolic resin and pyrolytic liquids are given in Table 2. Among the three liquids, phenolic resin had the highest density and the highest viscosity. Between the two pyrolytic liquids, poppy capsule pulp derived pyrolytic liquid had a higher density and higher viscosity.

Table 2. The physical properties of liquids

Properties	Waste Tire Pyrolytic Liquid	Poppy Capsule Pulp Pyrolytic Liquid	Phenolic Resin
Density (kg/m3)	945	998	1220
Kinematic Viscosity (cST)	398	545	2200

The chemical compounds in phenolic resin and pyrolytic liquids were selected from GC-MS chromotograms. The chemical compounds which had the peaks with a high degree of probability

(≥80%) and peak areas around or greater than 0.1 % were selected and evaluated. The relative percentages of phenols, aromatics, oxygene containing compounds, alkanes, alkenes, alkynes, and sulphur containing, chlorine containing, and nitrogen containing compounds are given in Table 3.

According to the results of the chemical analyses, phenolic resin consisted mostly of phenolic compounds and aromatics, and it contained little amount of oxygen containing compounds (1.58%). As phenolic resin, poppy capsule pulp pyrolytic liquid mostly consisted of phenolic compounds (40.35%). However, it contained much more oxygenated compounds (36.33%) than resin (1.58%). Waste tire pyrolytic liquid did not contain any phenolic compounds, but it mostly consisted of aromatics (66.80%). It contained oxygenated compounds (14.08%) and a little amount of sulphur containing compounds (0.88%) left after acidic extraction.

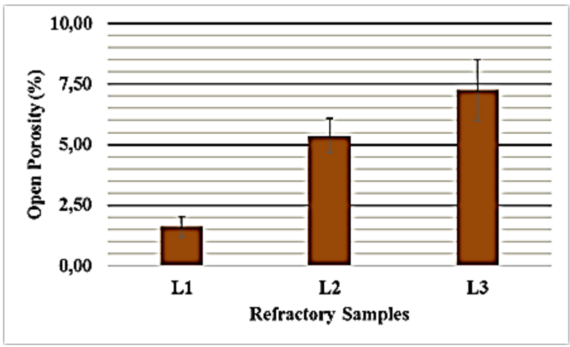
Table 3. Relative percentages of groups of chemical compounds in liquids determined by GC-MS

Groups of chemical compounds	Relative Percentages (%)		
	Phenolic Resin	Poppy Capsule Pulp Pyrolytic Liquid	Waste Tire Pyrolytic Liquid
Phenols	58.41	40.35	0.00
Aromatics	39.99	11.81	66.80
Oxygenates	1.58	36.33	14.08
Alkanes	0.00	3.81	5.49
Alkenes	0.00	1.28	3.58
Alkynes	0.00	1.96	1.08
S-Containing compounds	0.00	0.00	0.88
Cl-Containing compounds	0.00	0.51	3.42
N-Containing compounds	0.00	3.96	4.67

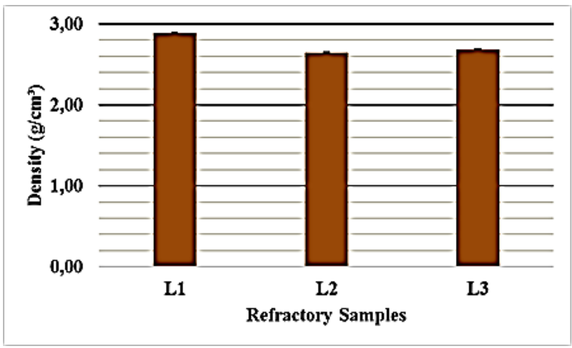
3.2 Open Porosities and Densities of MgO-C Refractories

Open porosities and densities of compositions, which were prepared by incorporation of graphite, waste tire pyrolytic liquid, poppy plant pyrolytic liquid and phenolic resin in MgO at specific ratios, are given in Figure 1.

The highest density value was achieved in the L1 sample that was obtained by graphite and resin. The samples produced by pyrolytic liquids had density values that were very close to each other. However, open porosity values of L2 and L3 samples were very different. The L3 sample which contained poppy capsule pulp pyrolytic liquid had higher open porosity than the sample obtained by waste tire pyrolytic liquid (L2). The use of resin caused the L1 sample to have the lowest open porosity. Occurrence of oxygenated volatile compounds (alcohols, esters, ketons, ethers, and free acids), caused formation of porosity during tempering process. Because poppy capsule pulp pyrolytic liquid had the highest amount of oxygenated volatile compounds, L3 refractory had the highest open porosity. Porosity increased with the increasing amount of oxygenated compounds in binder liquids.



(a)



(b)

Figure 1. a) Open porosity, b) densities of MgO-C refractory materials.

3.3 Cold Crushing Strengths of MgO-C Refractories

The Cold Crushing Strength (CCS) values of compositions in the shape of 50mm×50mm×50mm (width×length×height) square prism are shown in Figure 2. The resin containing sample had the highest strength. Among pyrolytic liquid containing samples, L3 obtained by poppy capsule pulp pyrolytic liquid had a higher density than L2 sample which contained waste tire pyrolytic liquid.

Because the viscosity of poppy capsule pulp pyrolytic liquid was higher than waste tire pyrolytic liquid (Table 2), it wetted MgO grains much more effectively than the latter. Effective wetting of MgO grains means effective binding of grains with graphite causing higher cold crushing strength.

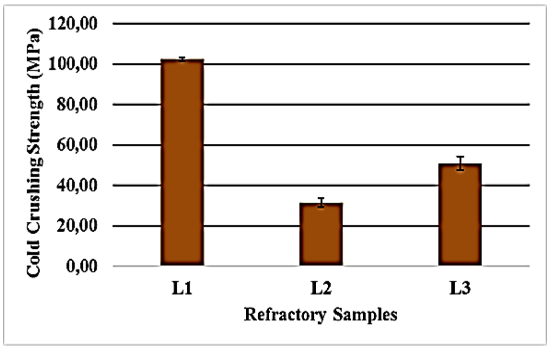


Figure 2. Cold crushing strength (CCS) values of refractories

3.4 Microstructure and Fracture Surface Characterizations by SEM

Backscattered electron images of L1, L2 and L3 materials are given in Figure 3. In all SEM images, black regions indicated porosities and, white regions indicated the compounds of Al, Si, Ca coming from magnesia as impurities. Thermal expansion coefficient mismatch between of MgO and graphite caused microcracks especially in the MgO grains in the structure.

According to back scattered electron image of L1 refractory material produced by adding graphite and resin, MgO grains could be surrounded by graphite flakes and resin, well bonded and created more dense structure than refractories produced by pyrolytic liquid addition (Figure 3 (a)).

In L2 refractory material produced by the use of waste tire pyrolytic liquids as a binder, even though pyrolytic liquid could wet graphite and MgO grains, those grains could not be well bonded. It was observed that L2 had the highest amount of porosities and microcracks in the structure. Therefore, the lowest density was achieved in this material (Figures 3(b)).

In L3 refractory material produced by the use of poppy capsule pulp pyrolytic liquids as a binder, graphite and MgO grains were better bonded, also less amount of porosities and microcracks were observed than that of L2 (Figure 3(c)) due to the presence of phenolic compounds in pyrolytic liquid of poppy capsule pulp.

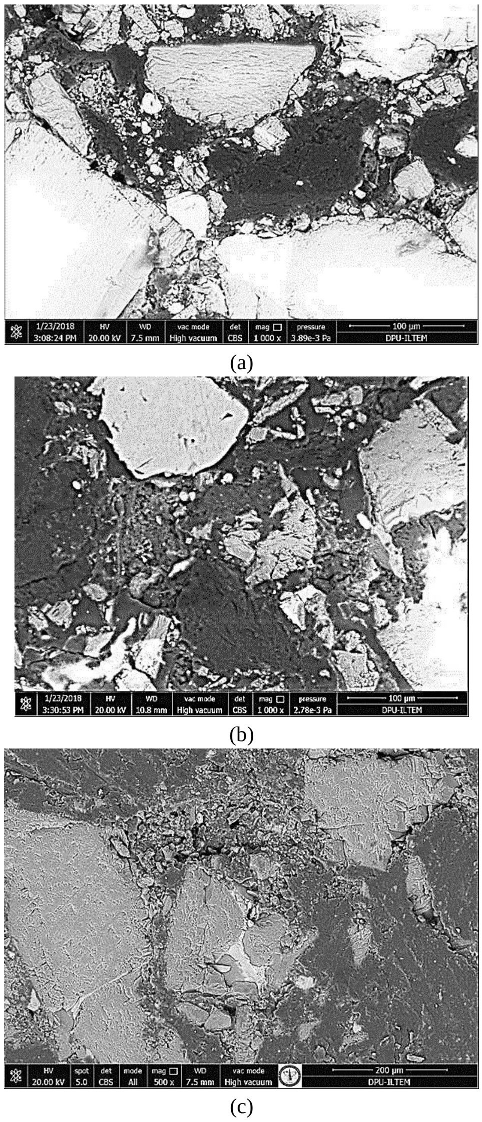
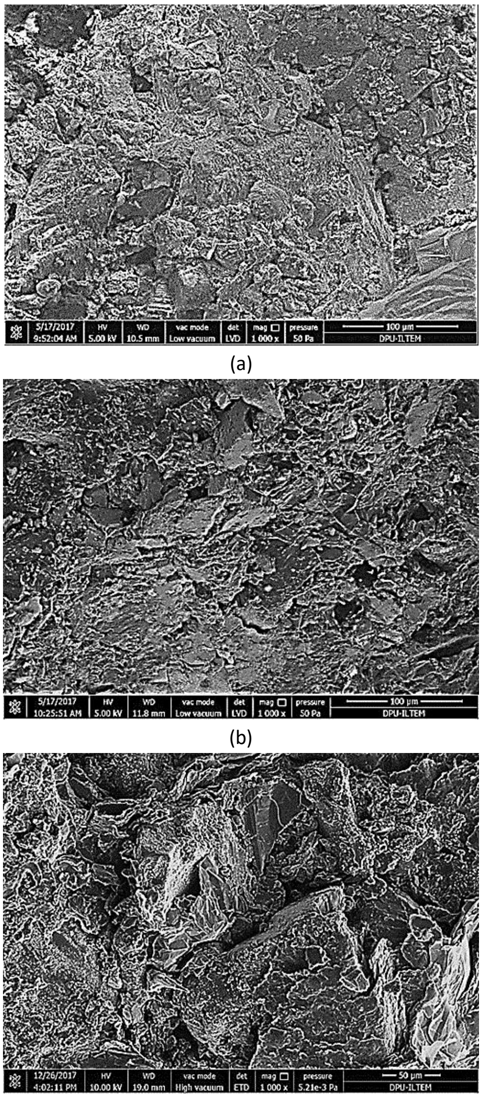


Figure 3. Back Scatterred Electron (BSE) images of samples (×1000) after thermal shock test. a) L1 refractory material b) L2 refractory material c) L3 refractory material.

According to images of fracture surfaces (Figure 4), for L1 and L3 refractories, it was observed that either intergranular or transgranular fracture types were observed in coarse and medium MgO grains and, small MgO grains, respectively. However, intergranular fracture type was dominant in L2 refractory. Higher strength values in L1 and L3 refractories than that of L2 were observed due to the presence of either intergranular or transgranular fracture types.



(a) (b) (c)

Figure 4. Secondary Electron (SE) images of fracture surfaces of MgO-C refractory materials (×1000)

4. Conclusions

Phenolic resin and poppy capsule pulp pyrolytic liquid consisted of phenolic compounds whereas waste tire pyrolytic liquid did not. The highest density and strength values were achieved in the L1 sample that was obtained by graphite and resin. The samples produced by resin and poppy capsule pulp pyrolytic liquid had lower porosities and higher CCS than L2 sample, which was incorporated with pyrolytic liquid obtained from waste tire. According to the results of this study, it was observed that valorization of biomass poppy capsule pulp as a source for organic and green binder for MgO-C refractory production.

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