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Effect of Demineralization Process on the CO_2 Gasification of Lignite

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Lignite,
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Abstract: The effect of different demineralization process on CO_2 gasification of cokes obtained from Karaman / Ermenek lignite at different temperatures was investigated in this study. 10% and 20% hydrochloric acid (HCl), nitric acid (HNO_3) and sulfuric acid (H_2SO_4) solutions were used in the demineralization process. The demineralized lignite samples were subjected to coking process at the temperatures ranging between 500°C-800°C, and the reaction capabilities of the obtained cokes in the gasification reaction with CO_2 at the temperatures ranging between 900°C–975°C were determined. The reaction capabilities of the demineralized lignite samples during CO_2 gasification were observed to be lower than those of the samples untreated with acid. In addition, it was observed that the reaction capabilities of cokes increased with increasing of coking temperature.

Demineralizasyon İşleminin Linyitlerin CO_2 ile Gazlaştırılmasına Etkisi

Anahtar Kelimeler
Linyit,
Demineralizasyon,
Gazlaştırma

Özet: Bu çalışmada, Karaman / Ermenek linyitine uygulanan demineralizasyon işleminin, farklı sıcaklıklarda elde edilen kokların CO_2 ile gazlaştırılmasına etkisi incelenmiştir. Demineralizasyon işleminde, % 10'luk ve % 20'lik hidroklorik asit (HCl), nitrik asit (HNO_3) ve sülfürik asit (H_2SO_4) çözeltileri kullanılmıştır. Demineralize edilmiş linyit numuneleri, 500°C-800°C sıcaklık aralığında koklaştırma işlemine tabi tutulmuş ve elde edilen kokların, 900°C–975°C aralığındaki sıcaklıklarda CO_2 ile gazlaştırma reaksiyonundaki tepkime yetenekleri belirlenmiştir. Mineralleri uzaklaştırılmış numunelerin CO_2 ile gazlaştırılmaları sırasındaki tepkime yeteneklerinin, asitlerle işlem görmemiş numunelerinkine göre daha düşük olduğu gözlenmiştir. Ayrıca, asitlerle yıkanmış numunelerin maruz bırakıldığı koklaştırma işleminin sıcaklığı arttıkça, kokların tepkime yeteneğinde de artış gözlenmiştir.

1. Introduction

Although the energy requirement of the world is showing a significant increase due the population growth and industrialization whereas the energy resources are gradually decreasing. Utilization of fossil fuels such as coal has gained again great importance in oreder to reduce energy deficit. Coal reserves are much more than the oil reserves and coal has the highest share after petroleum within the world primary energy [1, 2].

Turkey has approximately 13.9 billion tons lignite reserves whereas limited amount petroleum and natural gas reserves [3].

96% Turkish lignites have more than 20% ash and approximately 85% of these lignites have more than 20% moisture. The sulfur content of Turkish lignites vary between 0.4-9.3% which values are quite big than acceptable sulphur content of the fuel standards. In addition, approximately 80% of the Turkish lignites have a heating value below 2500 kcal/kg [4]. Regarding these quantities, it can be concluded that most of the Turkish lignites have poor quality. The burning of these lignites cause low combustion efficiency and air pollution problems [5, 6].

In addition to this, the fact that lignites have high ash and sulfur contents limits their effective use with carbonization, combustion, gasification and liquefaction processes. In recent years, studies for the evaluation of low-quality fuels are increasing because the high quality coal reserves are gradually decreasing. Demineralization and desulphurization are common process to obtain clean fossil fuels from low rank coals [7–12].

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There are various minerals in the coal structure. All of the inorganic components in the coal structure are defined as minerals [13]. The mineral matter and sulfur compounds present in the coal cause to decrease heating value of coal, to create environmental pollution problems and another undesired corrosion problems in the combustion units. No matter how effective the coal preparation techniques are, a significant amount of mineral matter is always remained in the coal and plays an important role during the use of coal.

The liquefaction, gasification and pyrolysis processes are significantly affected by the amount, type and distribution of the mineral matter in the coal structure [14, 15]. Therefore, the mineral matters should be removed from the coal.

The demineralization of coals can be performed by using both physical and chemical methods. Physical methods depend on the organic structure of the coal and the physical properties of minerals in the structure. Although simple physical methods are sufficient for the demineralization process for many fuel types, but clean demineralized coals can only be obtained by chemical methods [16].

It is important to know the effect of demineralization process on the coal structure and on the effect of reactivity of parent coal. A typical demineralization process is the washing of the coal with aqueous acids [17-19]. This operation increases the solubility and depolymerization reactivity of coals especially in the coal conversion processes such as gasification and liquefaction [20]. The washing of coal with acidic solutions causes the improvement of coal properties such as solubility and coking.

The purpose of this study is determined the effect of mineral matter on the gasification process. The demineralized lignite samples by using different acids were subjected to coking process at the temperatures between 500°C-800°C, and the reaction capabilities of the obtained cokes during the gasification reaction with CO_2 at the temperatures between 900°C–975°C were determined.

2. Material and Method

2.1. Lignite samples

The lignites of Karaman / Ermenek region obtained from TKI (Turkey Coal Enterprises) were used in the experiments. First, the lignite was ground to the small pieces and then crushed by grinding 0.3-2 mm in size. The samples were dried at room temperature and then stored in reserved containers to be used in the experiments.

The chemical and elemental analyses of lignite samples were performed according to ASTM standards [21, 22] and the analysis results are given in Table 1.

2.2. Demineralization process

Lignite samples were washed with 10% and 20% HCl, HNO_3 and H_2SO_4 solutions at ambient temperature. Then the lignite-acid solution mixtures were filtered, and the acid remained in samples were removed by washing with distilled water and dried for about 2 hours at 110°C. The dried samples were stored and used in the gasification experiments.

Table 1. Chemical and elemental analysis of Karaman / Ermenek lignite

Linyit type	Chemical analysis (%)				
	Moisture	Ash	Volatile matter	Fixed carbon	
Karaman / Ermenek	14.5	21.0	44.5	20.0	
	Elemental analysis (%)				
	C	H	N	S	O
Karaman / Ermenek	73.63	4.90	0.50	3.80	17.17

2.3. Coking process

The experimental setup used for coking experiments is shown in Figure 1. A certain amount of lignite with grain size between 0.3-2 mm was into the tubular reactor and the reactor is placed horizontally into the furnace The nitrogen gas is passed through the system until no oxygen exist in the reactor (30 minutes. Then, the furnace is heated up to the required coking temperature and kept at the final temperature (≈ 4 hours) until the end of tar output. The amounts of coke in the tubular reactor are determined after waiting for furnace to cool down to the room temperature.

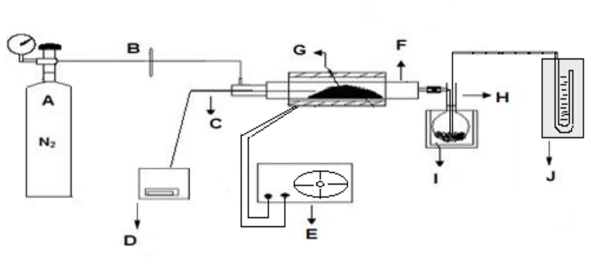

Figure 1. The schematic diagram of the coking system. (A) Nitrogen bottle, (B) float flowmeter, (C) thermocouple, (D) the temperature controller. (E) variac, (F) reactor, (G) coking furnace, (H) tar collecting vessel, (I) cooling unit, (J) manometere

2.4. CO_2 gasification of cokes

2.4.1. Experimental system

The schematic diagram of the gasification system was given in Figure 2. The system consists of the parts mentioned below.

- The tubular reactor in which the coke is gasified, the furnace by which the reactor is heated and the system controlling the temperature
- CO_2 tube, valves adjusting the gas flow rate, flow meter, manometer
- The trap serving for retaining the liquid and possible solid particles in products
- IR-absorption device that can measure CO concentration
- Recorder

Reactor is made of 310SS stainless steel tube of 2.5 cm diameter. A tube which was 5 cm long and 0.8 cm in diameter was welded to the lower part of the tubular reactor, and its end was connected to traps with a hose. There are the chamber where the solid sample would be placed, thermometer and CO_2 input in this upper part. Before starting the experiment, a layer is formed by placing glass-fibre to the middle of the tubular reactor. A defined amount of sample is put into the chamber. After the reactor temperature is adjusted to the desired value by the adjustable furnace, the chamber cover is opened and the fuel in the chamber is dropped into the reactor which is swept with CO_2 gas. During the experiment, the gasification temperature is measured with thermocouples extending up to the middle of the coke layer and recorded. A rapid decrease in temperature is observed when solid fuel is dropped into the reactor which is held at a certain gasification temperature. The temperature turns back to its initial value within about 4-5 minutes. Meanwhile, CO_2 gas which was passed through the tubular reactor reacts with the solid $C + CO_2 \rightarrow 2CO$ (Boudouard reaction). Then, the percentage of CO in the product gas going to IR-absorption device through the traps is continuously identified and recorded.

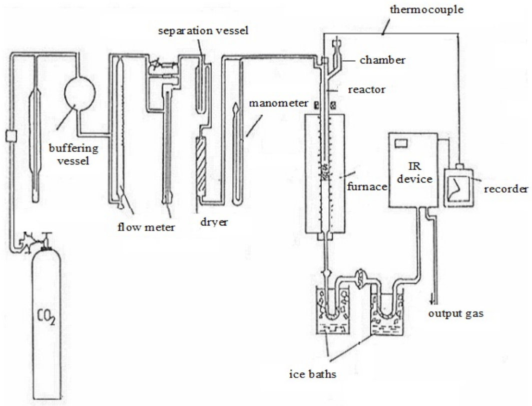

Figure 2. The schematic diagram of the gasification system

2.4.2. Gasification experiment

About 5 g acişd-washed sample is placed into the chamber on top of the reactor. The reactor is placed into the furnace, and it is heated up to the desired gasification temperature. Then, the sample to be gasified is dropped into the tubular reactor through which CO_2 gas at a certain flow rate was passed, and this moment is recorded as t = 0 time. The experiments were performed in a way the CO concentration would remain between 20-40% by setting the gas flow rate because the degree of Boudouard reaction might change by the amount of carbon monoxide in the product gas. After 30 minutes, CO_2 tube is closed and the gas supply is ceased, and the reactor is taken out of the furnace and cooled with spraying air. The residual coke that remains in the reactor is weighed, and its mass is recorded. The temperature of the coke and the CO concentration in the gas flow coming out of the reactor are continuously recorded during the experiment.

2.4.3. Evaluation of the experimental data

The reaction rate is given as follows by accepting that the reaction of carbon in the coke with CO_2 occurred in the first degree compared to CO_2 [23]:

$$\frac{dn_{CO2}}{dt} = \frac{dn_c}{dt} = -k_m \times m \times C_{CO2} \qquad (1)$$

$$d\dot{n}_{CO2}(x) = -k_m \times d_m \times C_{CO2} \qquad (2)$$

Where, m is the amount of coke (g), C_{CO2} is the concentration of CO_2 (mol/cm^3), k_m is the mass based reaction rate constant (cm^3/g s).

The following equation can be written for a differential coke layer with height of dx and mass of d_m.

$$d_m = (m/L)d_x \qquad (3)$$

When this equation is put in equation (1)

$$d\dot{n}_{CO2}(x) = d\left[\dot{V}(x) \times C_{CO2}(x)\right] \qquad (4)$$

Where, V(x) is the volumetric flow rate (cm^3/s) of gases at x point of a layer at the temperature of T, C(x) is the concentration of CO_2 gas at this point and L is the length of cola layer.

$$d\left[\dot{V}(x) \times C_{CO2}(x)\right] = -k_m \times \frac{m}{L} \times d_x \times C_{CO2}(x) \qquad (5)$$

$$\dot{n}_{CO} = 2\left[\dot{V}_o \times C_o - \dot{V}_x \times C(x)\right] \qquad (6)$$

$$\dot{n}_{CO} = \dot{V}(x) \times C_{tot}(x) - \dot{V}(x) \times C(x) \qquad (7)$$

Although CO_2 concentration decreases along the coke layer, V(x) flow rate increases because the number of moles the gas doubles in Boudouard reaction. If the flow rate of CO_2 entering into the coke layer is taken as V_o, and its concentration is taken as C_o; it can be written as follows

$$\dot{V}(x) = \frac{2\dot{V}_o}{1+\frac{C(x)}{C_o}} V(x) = \frac{2V_o}{1+\frac{C(x)}{C_o}} \qquad (8)$$

If Equation 8 is put in the differential Equation 4 and its integration is taken over the *L*-long total coke layer, the following equation is achieved.

$$2In\frac{2\,{}^{C_L}/_{C_o}}{1+{}^{C_L}/_{C_o}}+\frac{1-{}^{C_L}/_{C_o}}{1+{}^{C_L}/_{C_o}}=-k_m\times{}^{m}/_{V_o} \qquad (9)$$

Where, C_L is CO_2 concentration in the gas exiting the reactor.

$$k_m = D_a\times\frac{V_o}{m}\times\frac{T}{T_o} \qquad (10)$$

$$D_a = k_m\times\frac{m}{V_o} \qquad (11)$$

Where, T is the temperature at which the experiment was performed (K), V_o (T_o) is the reaction rate at the ambient temperature (cm^3/s), T_o is the ambient temperature (K) and D_a is the dimensionless Damköhler number.

From the Equation 10, Damköhler number is calculated by using the measured concentrations of CO_2 and CO. Than by using the mass of lignite, Damköhler number and V(o) the reaction rate (k_m) values can be calculated.

3. Results

The coking process was performed by the heating of Karaman / Ermenek lignite at the temperatures of 500°C, 600°C, 700°C and 800°C in a nitrogen gas atmosphere. The cokes obtained here were named according to their coking temperature. The structure of the coal consists of intensively and tightly bonded aromatic ring units, aliphatic heteroatom bonds and functional groups bonding these units [24]. The volatile substances which are initially formed by breaking of aliphatic bonds and heteroatom bridges are separated from the structure because the weak bonds will be firstly ruptured with temperature increasing. The excessive increase in temperature causes more separation of substance from the structure during coking. Therefore, the amount of volatile substance remaining within the cokes obtained at high temperatures should be low.

The coke samples were reacted with CO_2 gas. Within 30-minute experimental period, the amount of CO in the resultant gas mixture was determined by IR-absorption device, and the reaction rates were calculated using above mentioned kinetic equations.

Arrhenius curves were plotted versus the gasification temperatures of the rate constants determined by the CO_2 gasification of 500°C, 600°C, 700°C and 800°C cokes and the same curves are plotted for the coke samples washed with 10% and 20% (HCl, HNO_3 and H_2SO_4) acid solutions. The gasification temperatures of all samples were at 900°C, 925°C, 950°C and 975°C.

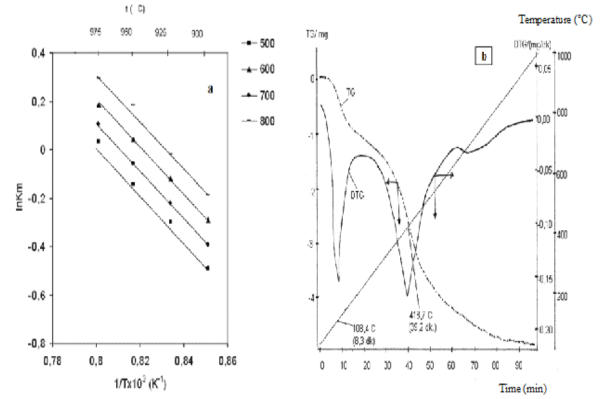

Figure 3. a) Arrhenius curve of gasification with CO_2 of cokes b) Thermal analysis diagram of the original lignite

Arrhenius curves of cokes at different temperatures are presented in Figure 3a. As it is seen from the curve, the reaction rate (the reaction capability) increases with increasing coking temperature and gasification temperature. This can be explained as follows: although the readily volatile components in the coal structure are separated as the temperature increases during the coking of coals, new pores are formed and the diffusion of CO_2 gas into the pore becomes easier. Thus, reactions occur both on the coal surface and in the pore. However, the reactivity of the 700°C coke is lower compared to 600°C coke. According the Figure 3b, reduction of mass loss at this temperature (700°C) leading the closure underlying pores and eventually the gasification rate decreases. Here, the lignite sample was heated from 20°C to 1000°C at a certain rate under nitrogen gas atmosphere, and the decrease in mass and the mass-deficit per unit time were plotted versus temperature. The mass loss observed around 700°C resulted from the fact that C–CO_2 reaction occurring at this temperature by the closure of the pores in the lignite structure occurred at a lower rate compared to 600°C and 800°C.

Arrhenius curves showing the reaction of the cokes, which were obtained from the lignite treated with 10% and 20% HCl solution at different temperatures with CO_2 are given in Figures 4a and 4b respectively. The change of the reaction capabilities of the cokes according to the temperatures at which they were obtained given in Figure 4a and the results of Figures 4a and 4b show similarity. However, the catalytic effect of carbonates, sulfides, iron, calcium, magnesium and aluminum cations on C–CO_2 reaction disappeared because these are removed from the lignite structure as a result of the treatment with HCl, and thus a decrease was observed in the reaction capabilities of the cokes obtained from the lignite washed with 10% and 20% HCl in their reaction with CO_2 compared to those of cokes obtained from untreated lignite. The weight loss observed in the coal by the process of washing with HCI is due to the cleavage of soluble mineral substances such as carbonates and sulfides (except pyrites) [25].

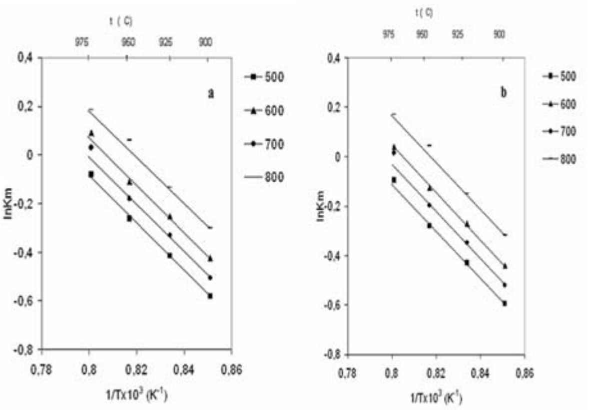

Figure 4. Arrhenius curves of cokes a) washed with 10% HCl solution b) washed with 20% HCl solution

Arrhenius curves of the cokes obtained from the lignite treated with 10% and 20% HNO_3 solution at different temperatures with CO_2 are given in Figures 5a and 5b respectively. The gasification rates of the cokes obtained from the lignites washed with 10% and 20% HNO_3 were found to be lower than the gasification rate of the unwashed cokes. Because the separation of mineral matters such as pyrites as a result of washing with HNO_3 probably caused a decrease in the gasification rate. Pyrite causes a catalytic effect on the original coal. From Figure 5a and Figure 5b, it is seen that washing with 20% HNO_3 solution has any significant different effect in the demineralization process compared to washing with 10% HNO_3 solution.

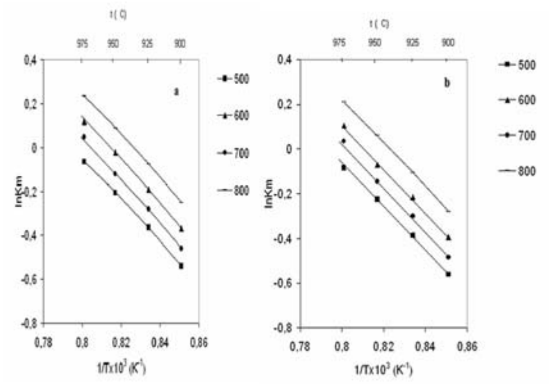

Figure 5. Arrhenius curves of cokes a) washed with 10% HNO_3 solution b) washed with 20% HNO_3 solution

The pyrite (FeS_2), which is commonly found in the coal structure as a mineral matter, reacts with sulphuric acid to form iron (III) sulfate by a two-stage reaction at high temperatures and in concentrated solutions. A significant amount of pyrite could remain in the coal structure after the sulfuric acid treatment. In a study carried out by Ralph et al, it was demonstrated that approximately 25% pyrite remained in the coal as a result of the elemental analysis [26]. Pyrite has the capability of reacting with dilute HNO_3 solution at low temperatures. For instance, it was determined that pyrite reacted with 5% aqueous HNO_3 solution at 75°C to form iron nitrate and elemental sulfur. The reactions between HNO_3 and pyrite are very complex and also sensitive to temperature and HNO_3 concentration [27].

Arrhenius curves of the cokes obtained from the lignite demineralized with 10% and 20% H_2SO_4 solutions are presented in Figures 6a and 6b, respectively.

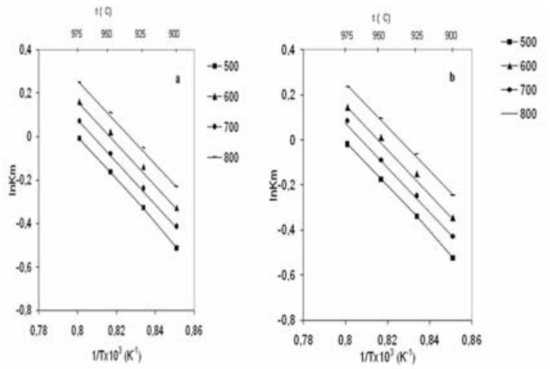

Figure 6. Arrhenius curves of cokes a) washed with 10% H_2SO_4 solution b) washed with 20% H_2SO_4 solution

When Figures 6a and 6b were compared with Figure 3a, the gasification rates of the cokes obtained from the lignites washed with 10% and 20% H_2SO_4 were found to be lower than the gasification rate of the cokes obtained from the original lignite. This can be explained as follows: many of the mineral matters in the coal are removed as a result of washing with H_2SO_4. But pyrite is not affected by washing with H_2SO_4. Thus, the separation of these minerals causes a decrease in the gasification rate. Their catalytic effects were eliminated by separating these minerals from the coal by washing with H_2SO_4. Thus, the gasification rate decreased compared to cokes obtained from the original lignite.

It is determined that CO_2 gasification reaction of the cokes obtained from the demineralized lignites progressed at a slower rate than the CO_2 gasification reaction of the cokes obtained from the untreated lignites.

The calculated reaction rate constants of the cokes obtained from Karaman / Ermenek lignite are given in Tables 2-5. When the gasification rates of the unwashed cokes at temperatures of 900°C, 925°C, 950°C and 975°C compared with reaction rates of cokes washed with acid solutions the reaction rates of washed cokes are lower than the unwashed sample.

4. Discussion and Conclusion

It can be concluded that the acid treatment of lignites removed the minerals from the coal structure and cause the decreasing of catalytic effect during the gasification. Therefore the reaction rates of untreated cokes are higher than the acid treated cokes. This observation is consistent with various studies in the literature.

Table 2. Calculated reaction rate constants of gasification with CO_2 at 900°C

Coking temperature (°C)	The reaction rate constants at 900°C (k_m : cm^3 / g s)						
	Original lignite	Lignite washed with 10% HCl	Lignite washed with 20% HCl	Lignite washed with 10% HNO_3	Lignite washed with 20% HNO_3	Lignite washed with 10% H_2SO_4	Lignite washed with 20% H_2SO_4
500	0.61	0.56	0.55	0.58	0.57	0.59	0.59
600	0.75	0.65	0.64	0.69	0.67	0.72	0.71
700	0.67	0.60	0.59	0.63	0.61	0.66	0.65
800	0.83	0.74	0.73	0.78	0.75	0.79	0.78

Table 3. Calculated reaction rate constants of gasification with CO_2 at 925°C

Coking temperature (°C)	The reaction rate constants at 925°C (k_m : cm^3 / g s)						
	Original lignite	Lignite washed with 10% HCl	Lignite washed with 20% HCl	Lignite washed with 10% HNO_3	Lignite washed with 20% HNO_3	Lignite washed with 10% H_2SO_4	Lignite washed with 20% H_2SO_4
500	0.74	0.66	0.65	0.69	0.68	0.72	0.71
600	0.89	0.78	0.76	0.83	0.81	0.87	0.86
700	0.79	0.72	0.71	0.76	0.74	0.79	0.77
800	0.98	0.87	0.86	0.93	0.90	0.95	0.94

Table 4. Calculated reaction rate constants of gasification with CO_2 at 950°C

Coking temperature (°C)	The reaction rate constants at 950°C (k_m : cm^3 / g s)						
	Original lignite	Lignite washed with 10% HCl	Lignite washed with 20% HCl	Lignite washed with 10% HNO_3	Lignite washed with 20% HNO_3	Lignite washed with 10% H_2SO_4	Lignite washed with 20% H_2SO_4
500	0.86	0.77	0.75	0.81	0.79	0.85	0.84
600	1.04	0.89	0.88	0.98	0.93	1.02	1.01
700	0.94	0.83	0.82	0.89	0.86	0.92	0.91
800	1.19	1.06	1.04	1.09	1.06	1.12	1.09

Table 5. Calculated reaction rate constants of its gasification with CO_2 at 975°C

Coking temperature (°C)	The reaction rate constants at 975°C (k_m : cm^3 / g s)						
	Original lignite	Lignite washed with 10% HCl	Lignite washed with 20% HCl	Lignite washed with 10% HNO_3	Lignite washed with 20% HNO_3	Lignite washed with 10% H_2SO_4	Lignite washed with 20% H_2SO_4
500	1.03	0.92	0.91	0.94	0.92	0.99	0.98
600	1.20	1.06	1.04	1.13	1.11	1.16	1.17
700	1.11	1.03	1.01	1.05	1.03	1.07	1.09
800	1.34	1.20	1.18	1.26	1.23	1.28	1.26

The weight loss of demineralized lignite during the coking process is smaller than weight loss of untreated lignite because of some substances are previously removed from the lignite structure by acid-washing.

In addition, in the process of washing with 10% HCl acid applied to 500°C coke, a higher degree of demineralization was obtained than the degree of demineralization which was obtained by washing with 10% HNO_3 or 10% H_2SO_4 (10% HCl : 45.03% ; 10% HNO_3 : 39.05% ; 10% H_2SO_4 : 35.16%).

According to the obtained results, HCI was found to be more effective acid than HNO_3 and H_2SO_4 in the demineralization process. Therefore, this acid can be used alone for the demineralization of coals. When all figures were examined, it is seen that the reactivity of cokes increases up to 800°C. The reactivities of the cokes obtained from 500°C up to 800°C are gradually increasing readily volatile components are separated from the coal structure with the increase of temperature during the coking of Karaman / Ermenek lignite, and new pores are formed or it becomes easier to enter into the pores. However, the reaction capability of 700°C coke with CO_2 was observed to be lower than the reaction capability of 600°C coke. This can be explained by the constriction of the pores and surface area becomes smaller and entering of CO_2 into the pores become more difficult and reactivity of coke decreases.

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