Purification of Zinc Oxide Using Direct Thermal Process by Petroleum Coke

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Abstract

The present investigation is concerned for the purification of impure zinc oxide (80-85 wt %) by using petroleum coke (carbon content is 76 wt %) as reducing agent for the impure zinc oxide to provide pure zinc vapor, which will be oxidized later by air to the pure zinc oxide.
The operating conditions of the reaction were studied in detail which are, reaction time within the range (10 to 30 min), reaction temperature (900 to 1100 oC), air flow rate (0.2 to 1 l/min) and weight percentage of the reducing agent (petroleum coke) in the feed (14 to 30 wt %).
The best operating conditions were (30 min) for the reaction time, (1100 oC) for the reaction temperature, (1 l/min) for the air flow rate, and (30 wt %) of reducing material (petroleum coke) in the feed.
Under the above conditions, conversion of zinc oxide was (68.12 %) and the purity of the produced zinc oxide was (97.85 %) by using petroleum coke as reducing material.

Introduction

Zinc oxide (ZnO) is commercially the most important chemical compound of zinc. It is a fluffy, white powder, hexagonal crystal with exceptional and unique properties. Having a specific gravity (sp.gr.) of (5.68) and molecular weight (M) of (81.38 gm/gmol.), it sublimes at (1800 oC), is insoluble in water, and soluble in strong alkali solutions and acids. These distinct properties are utilized in many types of applications such as agriculture, ceramics, chemicals, paints, photocopying and rubber industries, the largest consumer of (ZnO) is the rubber industry (1).

The zinc oxide is produced by two thermal methods, in addition to wet (chemical) method. The two thermal methods are known as the direct and indirect, depending upon whether the raw material was zinc oxide in the form of calcined ore or drosses, or metallic zinc. As usual in the zinc industry a number of different types of furnaces have been developed to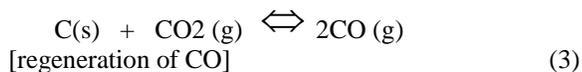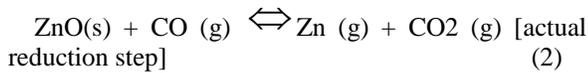 exploit each of the thermal methods (2). The indirect (French) process is historically the older, but today is used to produce only about one-half as much zinc oxide as the direct (American) process. French process zinc oxide is purer and finer than American process zinc oxide but French process is more costly than American process. The chemical (wet) process is much costly compared with the thermal processes, so it is not used largely in the industrial field (3).

Very few studies have been made on the reduction of zinc oxide or the oxidation of zinc vapor as shown below.

In 1917, Bodenstein (2,4,5) showed that the reduction of zinc oxide by carbon as follows:

$$ZnO(s) + C(s) \Longleftrightarrow Zn(g) + CO(g) \qquad (1)$$
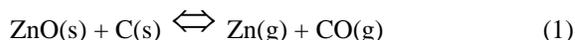
Proceeded by two successive gas-solid reactions which were readily reversible:

ZnO(s) + CO (g) $\Longleftrightarrow$ Zn (g) + CO2 (g) [actual
reduction step]   (2)

C(s) + CO2 (g) $\Longleftrightarrow$ 2CO (g)
[regeneration of CO]   (3)

The first thorough thermodynamic study of this
reduction was carried out by C.G. Maier (6) and his
colleagues at the U.S. Bureau of Mines. They
specified the temperature at which continuous
reduction of zinc oxide could be begin, and the
proportions of zinc vapor, carbon monoxide and
carbon dioxide which would exist at all temperatures
of interest in practical. The reduction of (ZnO) by
carbon cannot take place except above the boiling
point of zinc (907 ℃) so that the zinc product of the
reduction process is always in the vapor phase. The
reaction (3) is the slower than the reaction (2) below
about (1100 ℃) and hence controls the rate of
reduction in most commercial processes. Above
(1100 ℃), the rates of diffusion and heat transfer
predominate as rate-controlling factors.

Chen (7) studied the effect of the gas flow rate, grain
size, molar ratio of (C/ZnO), solid sample height,
initial bulk density and reaction temperature on the
reaction rate of the carbothermic reduction of pure
zinc oxide with carbon powder under a nitrogen
atmosphere (at 1 atm). Solid reactants in the
predetermined proportions were then mixed in a V
blender and then transferred to a cylindrical quartz
crucible and Nitrogen was flowed over the solid
sample and the conversion of zinc oxide and carbon
as well as the yield of zinc were determined. The
weights of solid samples were in the range of (5*10-4
to 1.5 *10-3 Kg). The operating variables studied are
shown below:

 1. (C/ZnO) molar ratio (1.0, 1.5, 2.0, 2.5)

 2. Carbon grain size (5, 39, 414), (*107 m).

 3. Zinc oxide grain size (5, 39, 414), (*107 m).

 4. Solid sample height (0.005, 0.01.0.015, 0.02), (m).

 5. Initial bulk density (ρ) (216.7, 336.5, 454.3,
570.4), (Kg/m3).

 6. Reaction temperature (1073, 1173, 1273, 1373,
1423), (K).

 7. Nitrogen gas flow rate (0.167, 0.833, 1.25,
1.67)(*105 m3/s).

Chen found that the conversion of zinc oxide could be
increased by increasing the molar ratio of (C/ZnO),
height of solid sample, density of solid sample or
reaction temperature and also found that the
conversion of zinc oxide could be increased by
reducing the grain size of zinc oxide and carbon or the
nitrogen gas flow rate.

 Both Clarke and Fray (8,9), and Stott and Fray (10)
studied the oxidation of zinc vapor according to the
reverse of reaction (2). The flow technique and
carbon monoxide, argon or nitrogen, with or without
additional carbon dioxide mixtures were used with a
temperature range (600-900 ℃) and experimental
apparatus consisted of a flow reactor and multi
temperature zones, resistance furnace in these
investigations. Under the reaction conditions
investigated two distinct reaction regimes were
observed; in both cases the reaction rate was found to
be controlled by surface chemical reactions as
opposed to gas phase diffusion. Below (800 ℃), the
reaction rate at any given temperature was found to be
controlled by prevailing excess zinc partial pressure
(the surface adsorption of zinc). For this regime a
massive oxide deposit with a grain size in the range
(5-20 μm) and typical reaction rates of (1-3 * 10-7
mol cm-2 s–1) were observed. In contrast, above (800
℃) and the carbon monoxide partial pressure in
excess of (0.2 atm), the reaction rate was found to be
strongly dependent on the prevailing carbon
monoxide concentration, with the carbon monoxide
appearing to retard the rate. For this regime the main
type of growth was found to have a much finer grain
size, in the range of (1-2 μm), with typical deposition
rates of (0.5-1.5 * 10-8 mol cm-2 s–1).

 These investigations were also extended by Clarke
and Fray (11) to the study of the oxidation of zinc
vapor in the mixed gas system (CO/CO2/
H2/H2O/Ar). The same experimental procedure was
adopted as in the simpler reaction system. Over the
temperature range investigated (600-900 °C), the
reaction rate was similar to that of the massive oxide
of (CO/CO2/Ar) system, and a finer grained deposit
was not observed. The reaction rate was again found
to be linearly dependent on the excess zinc partial
pressure, but a plot of reaction rate versus the
prevailing zinc partial pressure, did not in this case
produce a single straight line. Instead, it consisted of
two distinct straight-line portions. The two slopes
were found to be dependent on the gas composition,
and in particular on the relative abundances of the two
constituent reaction systems. For these gas mixtures
zinc oxidation will not be the sole reaction occurring,
since the interaction of the other constituent gases

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according to the "gas shift" reaction will also take place:

$$H_2 + CO_2 \Longleftrightarrow CO + H_2O \qquad (4)$$

Cox and Fray (12) studied the zinc vapor re-oxidation in the shaft of a Zinc-Lead Imperial Smelting Process in the mixed gas system ($CO/CO_2/H_2/H_2O$) by passing the gases through a heated quartz reactor containing zinc oxide pellets. The reverse of reaction (2) is the basic re-oxidation reaction. At temperature less than 750 ℃ (< 750 ℃), a distinct correlation was found between the deposition rate, excess zinc partial pressure and zinc oxide morphology. Furthermore, the deposition rate at temperatures more than 850 ℃ (> 850 ℃) was significantly greater than that at (< 750 ℃), the greater thermodynamic driving force losing out to the reduced temperature kinetic effect. Two distinct types of crystals were produced for the two temperature ranges, indicating two different mechanisms of formation.

Osborne, Rankin, McCarthy, and Swinbourne (13) studied the oxidation of zinc vapor in the (Zn-CO-CO2-N2) system for zinc partial pressure of (0.01 to 0.09 atm), carbon monoxide partial pressures up to (0.5 atm), and carbon dioxide partial pressures up to (0.6 atm) at (730 to 900 ℃). The experimental apparatus consisted of a flow reactor and a multi temperature zone furnace. The rate of oxidation of zinc was found to be a function of temperature and of the partial pressures of zinc, carbon monoxide, and carbon dioxide. It was autocatalytic with respect to carbon monoxide and independent of the total mass of zinc oxide deposited. The reactions occurring in parallel for this mechanism are the reverse of reaction (2.2) and the following reaction:

$$Zn(g) + CO_2(g) + CO(g) \Longleftrightarrow ZnO(s) + 2CO(s) \quad (5)$$
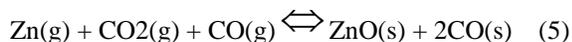
The aim of this study is to develop a laboratory system for the purification of an impure zinc oxide produced by-product (80-85%) in copper production process from brass scrap in Al-Shaheed Company, and obtain the best conditions (reaction time, reaction temperature, air flow rate and weight percentage of reducing agent in feed) for the purification process of an impure zinc oxide with high yield to achieve the required technical specifications of this oxide for the industrial purposes.

Experimental Work

Feed Briquetting

Generally, briquetting is a process for compressing fine materials into small blocks, or agglomerates, of sufficient mechanical strength to resist reasonable handling and weathering without deterioration. The main purpose of briquetting in the zinc oxide industry is to form strong briquettes composed of a homogenous mixture of the impure zinc oxide and the petroleum coke which will not impede the flow of gases or seriously disintegrate during the reducing operation. The briquetting process for preparing samples of the impure zinc oxide is shown in the following five principal steps: a) drying and grinding of the impure zinc oxide, (b) drying and grinding of the petroleum coke, (c) mixing and plasticizing the raw materials (impure zinc oxide and petroleum coke), (d) pressing of plastic mixture in the briquetting machine, and (e) drying of the material briquettes. The briquettes had cylindrical shape with dimensions (3mm diameter and 5mm length).
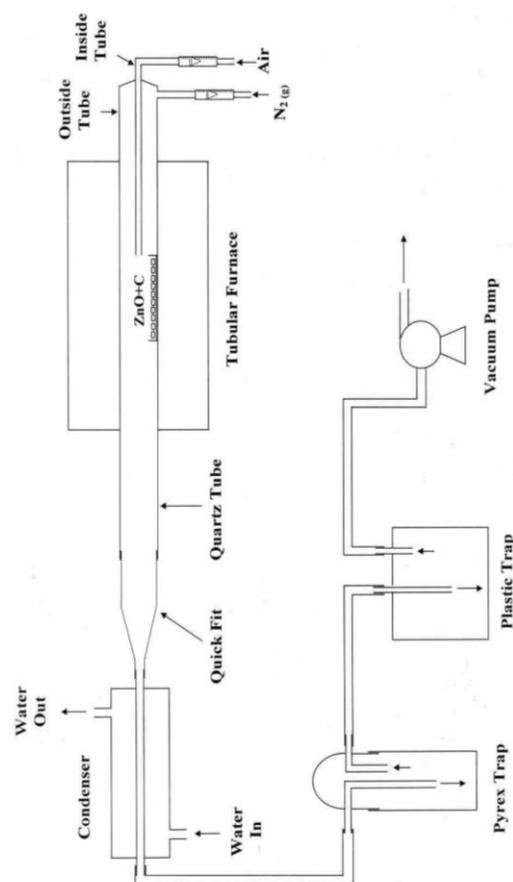

Fig.1 Schematic Diagram of the Experiment Laboratory Unit

Laboratory Experiment Unit

Figure (1) shows a schematic diagram of the laboratory experiment unit, which is employed for the purification of an impure zinc oxide by using the petroleum coke as reducing agent.

Raw Materials

The full description of the materials, which were used in this work, is shown below:

A. Laboratory Materials

1. Alumina (Al2O3)

A high-purity Alumina (99.999 %) was purchased from (BDH Limited Poole-England), with bulk density of (660 Kg/m3), and used as a binder in feed briquetting.

2. Hydrochloric Acid (HCl)

A concentrated hydrochloric acid (36 wt %) was purchased from (Hopkin and Williams Company-England), and was used as a cleaning solvent for the reactor quartz tube after each experiment.

B. Raw Materials

1. Impure Zinc Oxide

This material brought from Al-Shaheed General Company as a by-product from the copper production process. It contains (80-85 wt %) of zinc oxide and (15-20 wt %) of impurities.

2. Petroleum Coke

It was obtained from the Quiyarah Refinery (Iraq) and contained (76 wt %) carbon with high sulfur content about (7.5 %). It was used as

reducing agent for the impure zinc oxide in this research.

Five grams of feed briquettes are bedded evenly (in the same level (10 mm)) on the stainless steel boat. The sample is then pushed inside the isothermal zone of the (60 mm diameter quartz tube) by using stainless steel rod and boat. The electrical tubular furnace switching on and maintaining the furnace temperature at desired temperature (i.e. 900-1100 ºC) by using the automatic temperature controller. During this period (before the reaching to the desired temperature), the nitrogen gas is then allowed to flow at constant flow rate (0.1 l/min) to the (60 mm diameter quartz tube) through the rotameter (2) in order to ensure that only reduction reaction had occurred during this period without any oxidation reaction for zinc vapor. Stopping the nitrogen gas flow rate and switching on the vacuum pump to allow the air to flow at flow rate (0.2-1 l/min) to the (12.7 mm diameter quartz tube) through the rotameter (1) after the reaching to the desired temperature. When the inlet air is flowed through the tubular furnace, the oxidation reaction is started and zinc oxide fume is produced with reaction gases of carbon monoxide (CO), carbon dioxide (CO2) and air during this reaction. This product was cooled in the counter-current condenser by water. The decreasing of temperature in the condenser increased the oxidation reaction because the oxidation reaction is exothermic. So, the growth of zinc oxide crystals is occurred on the surface of condenser. Part of the produced zinc oxide was deposited on the surface of the inner pipe of the condenser and the other part was collected by the pyrex and plastic traps before the reaction gases reached the vacuum pump.

Produced Zinc Oxide Analysis

The purity of produced zinc oxide was determined by using the titration method. The solutions of (0.015 M) EDTA and (0.015 M) zinc chloride were prepared. Also, an (Eriochrome Black T) indicator solution was prepared by adding (0.1 gm) of this indicator in (25 ml) methanol. The weighted sample (0.2-0.25 gm) of the produced zinc oxide sample was dissolved in (250 ml) of concentrated hydrochloric acid (conc.HCl) to prepare the sample solution. After that, (25 ml) from the prepared sample solution was taken and put in the volumetric flask, then adding (50 ml) of the prepared EDTA and (10 ml) of concentrated ammonia solution to the flask in order to adjust the (PH) in the range (10-11). Also, drops of the (Eriochrome Black T) solution was added to the flask and finally, a titration with the prepared zinc chloride solution to a color change from blue to purple and volume of the titrated zinc chloride solution was (U). We repeated this titration without using the sample solution (Blank) and the volume of titrated zinc chloride solution was (B). The purity of the produced zinc oxide could be calculated by using the following relation:

$$\textbf{ZnO, Wt\%} = \frac{\textbf{(B}-\textbf{U)}\textbf{*m*1.245}}{\textbf{M}} \textbf{*100} \qquad (6)$$

Where:

B = Titrated zinc chloride solution volume without using sample solution

U = Titrated zinc chloride solution volume with usingsample solution.

m = 1.1(Correction factor).

M = Sample weight in (gm)= 0.2-0.25 gm.

1.245 = Ratio of molecular weights of zinc oxide to zinc.

Results and Discussion

Figure (2) shows the interaction effect of reaction time and reaction temperature on the conversion of zinc oxide. The conversion of zinc oxide had endured increasing function with respect to both reaction time and reaction temperature. This figure shows that the two variables (i.e., the reaction time and temperature) had concurred their influences, which resulted in an increase in conversion of zinc oxide with reaction time and temperature. This effect may be attributed to the reaction of zinc oxide reduction is endothermic.

Figure (3) shows the interaction effect between reaction time and air flow rate. In this figure, had endured increasing function with respect to both reaction time and air flow rate. This effect may be attributed to increasing the carbon dioxide gas concentration due to increasing the air flow rate.

Figure (4) shows the interaction effect between reaction time and weight percentage of petroleum coke in the feed .This figure shows that the conversion of zinc oxide had endured increasing function with respect to both reaction time and weight percentage of petroleum coke in the feed. This effect may be attributed to increasing the carbon monoxide gas concentration due to increasing the weight percentage of carbonaceous materials in the feed.

Figure (5) shows the interaction effect between reaction temperature and air flow rate. This figure shows that The conversion of zinc oxide had endured increasing function with respect to both reaction temperature and air flow rate. This effect may be attributed to the endothermic reaction of zinc oxide reduction and also to increasing the carbon dioxide gas concentration due to increasing the air flow rate.

Figure (6) represents the interaction between reaction temperature and weight percentage of petroleum

coke. This figure shows that The conversion of zinc oxide had endured increasing function with respect to both reaction temperature and weight percentage of petroleum coke. This effect may be attributed to the endothermic reaction of zinc oxide reduction and also more carbon monoxide gas is provided due to increasing weight percentage of petroleum coke in the feed.

Eventually, Figure (7) shows the interaction dependence between air flow rate and weight percentage of petroleum coke. This figure shows that that the conversion of zinc oxide had endured increasing function with respect to both air flow rate and weight percentage of petroleum coke. This effect may be attributed to increasing the concentrations of carbon monoxide and carbon dioxide gases due to increasing weight percentage of petroleum coke and air flow rate respectively.
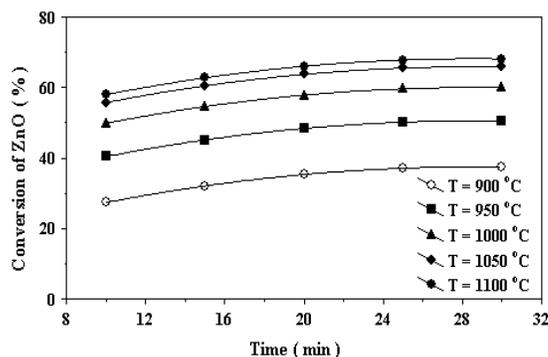

Fig. (2): Effect of Reaction Time on the Conversion of Zinc Oxide at various Temperatures using Petroleum Coke at 1 l/min and 30 wt% of Petroleum Coke in feed.
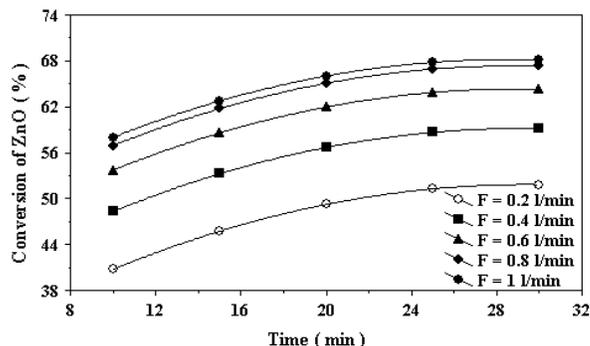

Fig. (3): Effect of Reaction Time on the Conversion of Zinc Oxide at various Air Flow Rates using Petroleum Coke at 1100 ^{o}C and 30 wt % of Petroleum Coke in feed.
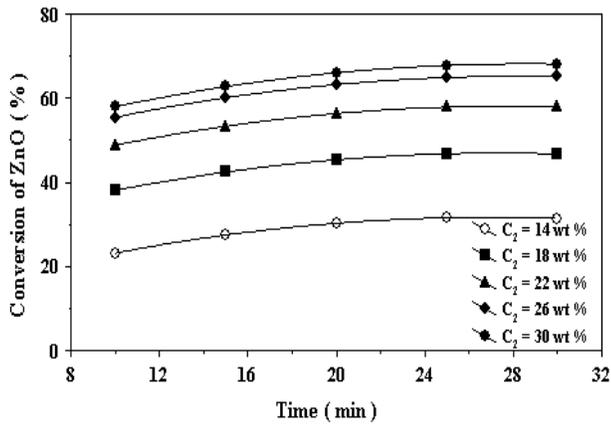
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Fig. (4): Effect of Reaction Time on the Conversion of Zinc Oxide at various Weight Percentages of Petroleum Coke in the Feed at 1100 ^{o}C and 1 l/min.
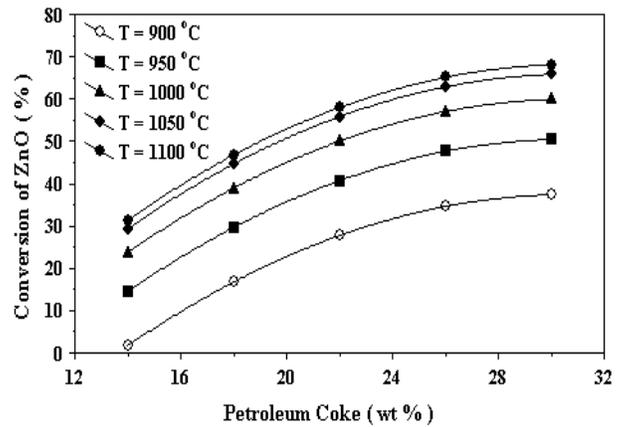

Fig. (6): Effect of the Weight Percentage of Petroleum Coke in the Feed on the Conversion of Zinc Oxide at various Temperatures at 30 min and 1 l/min.
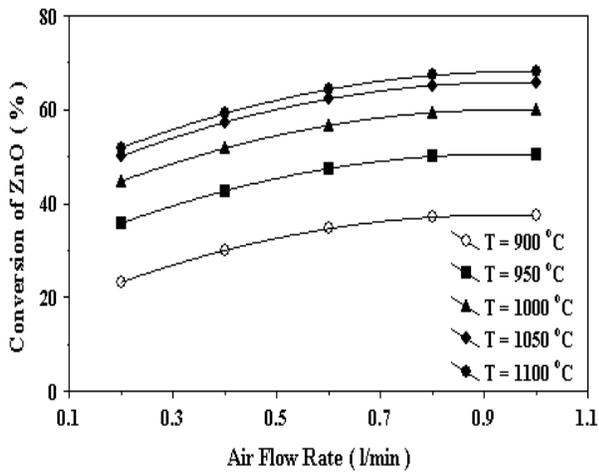

Fig. (5): Effect of Air Flow Rate on the Conversion of Zinc Oxide at various Temperatures using Petroleum Coke at 30 min and 30 wt % of Petroleum Coke in feed.
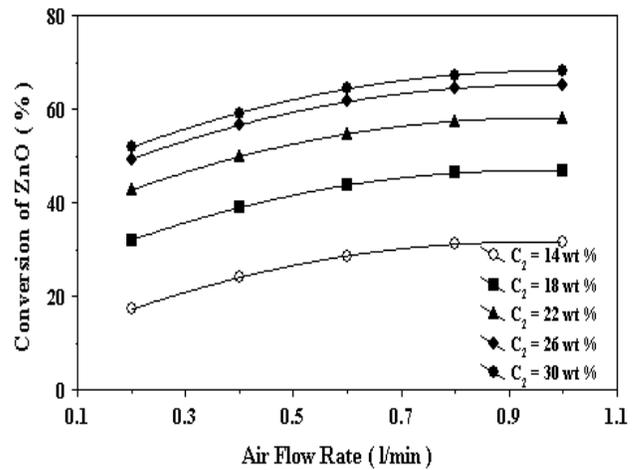

Fig. (7): Effect of Air Flow Rate on the Conversion of Zinc Oxide at various Weight Percentage of Petroleum Coke in the Feed at 30 min and 1100 ^{o}C.

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Conclusions

1- The best conditions for laboratory unit of zinc oxide purification by Using petroleum coke as reducing agent were as
   follows:
   i) Reaction time: 30 min (10-30 min).

   ii) Reaction temperature:1100°C(900-1100

      ^{o}C).

   iii) Air flow rate: 1 l / min (0.2-1 l / min).

   iv) Weight percentage of petroleum coke:

      30 wt % in the feed (14- 30 wt %).

2   As the above mentioned parameters attempted rising in this study, tend to increase the conversion (%) of zinc oxide.

Nomenclature

Sp. gr.	specific gravity	(-)
M	molecular weight	(gm/g mol)
X$_1$	reaction time	(min)
X$_2$	reaction temperature	(^{o}C)
X$_3$	air flow rate	(l/min)
X$_4$	weight percentage of petroleum coke in feed	(wt %)
N	number of Experiments	(-)
α	axial distance from the center point	(-)
q	number of Variables	(-)
Y	predicted value of the conversion of zinc oxide	(-)
y	observed value of the conversion of zinc oxide	(-)
t	reaction time	(min)
T	reaction temperature	(^{o}C)
F	air flow rate	(l/min)
C$_2$	weight percentage of petroleum coke in feed	(wt %)

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