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# Experimental Investigation of a Novel Reaction in Reduction of Sulfates by Natural Gas as a Reducing Agent

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***Abstract*****—**In a pilot plant scale of a fluidized bed reactor, a reduction reaction of sodium sulfate by natural gas has been investigated. Natural gas is applied in this study as a reductant. Feed density, feed mass flow rate, natural gas and air flow rate (independent parameters)and temperature of bed and CO concentration in inlet and outlet of reactor (dependent parameters) were monitored and recorded at steady state. The residence time was adjusted close to value of traditional reaction [1]. An artificial neural network (ANN) was established to study dependency of yield and carbon gradient on operating parameters. Resultant 97% accuracy of applied ANN is a good prove that natural gas can be used as a reducing agent. Predicted ANN model for relation between other sources carbon gradient (accuracy 74%) indicates there is not a meaningful relation between other sources carbon variation and reduction process which means carbon in granule does not have significant effect on the reaction yield.

***Keywords*****—**reduction by natural gas, fluidized bed, sulfate, sulfide, artificial neural network



## I. Introduction

A significant amount of substances extracted from mines should be reduced to be prepared for use as raw materials in factories. Great share of these reactions are conversion of sulfates into sulfides. On the other hand, natural gas is traditionally used as fuel. Development of new application of this natural resource is very essential. The aim of this experiment is to show the ability of natural gas to be used as a reductant. In order to set up experiments, sodium sulfate was used as an example substance (reduction of sodium sulfate to sodium sulfide is carried out).

Sodium sulfide is an inorganic chemical that has attained an important position in the organic industries. It is used as a reductant in the manufacture of amino compounds, and in preparation of many dyes. It is also consumed extensively in the leather industry. The most common sulfide production process is reaction between $H_2S$ and NaOH [2].

$$H_2S + 2NaOH \rightarrow Na_2S + 2H_2O \quad (1)$$

Sodium sulfide was produced traditionally from reduction reaction in which sodium sulfate reduced by carbon through following reaction [3]:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2 \quad (2)$$

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Conventional way of carbon supplying was mineral coal. Having use of this source accompanied with some meaningful disadvantages. Coal contains some impurities such as sulfur-compounds that release odorous environmental pollutant after reaction [4]. So this kind of processes has been gradually omitted during the years. The first reaction product is manufactured from expensive raw material and the second one has some environmental affects in contrast of environmental rules. On the other hand, use of natural gas as a carbon resource instead of source of energy is not usual.

As it was mentioned, in the traditional reaction coal is used as a reducing component to produce sodium sulfide. In this study, it is tried to regenerate the sulfates reduction by using natural gas as a carbon source instead of coal.

## II. Materials And Methods

### A. Elementary Reactions

Because of complicated condition of this kind of reactions, especially high temperature (around 1000˚ C); no one knows really for sure the elementary reactions. We postulate that the final reaction is occurred through of various elementary reactions such as [5],[6], and[3]:

$$CH_4 \rightarrow C + 2H_2 \quad (3)$$

$$C + O_2 \rightarrow CO_2 \quad (4)$$

$$CO_2 + C \rightarrow 2CO \quad (5)$$

$$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O \quad (6)$$

$$2H_2 + O_2 \rightarrow 2H_2O \quad (7)$$

$$Na_2SO_4 + CO \rightarrow Na_2S + 4CO_2 \quad (8)$$

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2 \quad (9)$$

Where the order of magnitude of each one is not specified.On the other hand this paper is concentrated to prove the reduction capability of natural gas, so a simple ANN is employed to show that the reduction will be occurred due to the totality of non- defined mentioned reactions.

### B. Equipment Selection

In order to set up the experiments two phase (gas-solid) reactor should be chosen to represent the observable changes. Fluidized bed reactor (FBR) has been previously applied successfully in high temperature condition and adhesive material [7].

In this reaction material reach to melting point due to the high temperature and it makes them sticky. In this condition an agglomeration phenomena is main problem in operating of process. In addition, fluidized condition makes continuous reactor discharging more comfortable [8]. More over very good heat and mass transfer coefficients and studied available hydrodynamic models are plus to attainable vital mentioned properties of fluidized bed. All of these features conduct us to select FBR for this reaction.

*C. Description of Pilot Setup*

Fig.1 illustrates sections and unit operation of the process. Because of the critical problems in equipment selection in laboratory size (e.g. Laboratory high pressure fan, cyclone and bag filter) it was decided to carry out these experiments in pilot scale. The reactor consists of 3 stages, a heat-resistant cylinder of 115 and 400 cm diameter and height respectively [9]. Stages were divided with a perforated plate distributor with 1.5% porosity [10]. Feed were charged continuously at top stage. Feed rate was about 450 Kg/hr of granules between 7 to 13mm in diameter. Granules component are described later. The fixed bed height was 30 cm. the top stage of reactor were used as a preheater and deduster. The reaction takes place at the second and third stages. The reactor was fitted rapidly with chromel-Alumel type temperature sensors and water tubes to sample the gas. Gas sampling tubes were connected to the suction pump through a long stainless steel water cooled pipe [11].

A set of infrared type analyzers to measure $CH_4$, $CO_2$, CO concentrations and paramagnetic type analyzer for $O_2$ were connected to the sampling pipe. The pilot burner was used for premixing of air and natural gas by injecting natural gas through a high porous perforated plate. The gas- air ratio was controlled by a PID system associated with a pneumatic valve. It was set up to control the temperature at the definite level and control the combustion of natural gas up to completion of this reaction and no more.

$$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O \tag{10}$$

This system controls air damper by CO content at the outlet of second stage. It should be noted that the burner ensures the security of the set up by completely burning gases at the outlet. The outlet gaseous mixture was ignited by a second burner which inserts natural gas and excess air in order to convert all carbons to CO2.

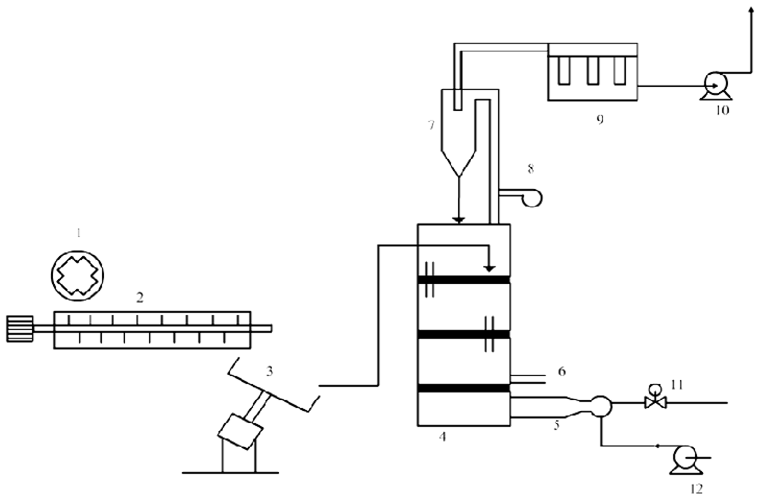


Fig. 1 Scheme of pilot plant:1-crusher 2- paddle mixer 3- disc granulator 4-fluidized bed reactor 5- burner 6- discharge pipe 7- cyclone 8- burner 9- bag filter 10- exhaust fan 11-control valve 12- fan

*D. Feed Preparation*

Solid feed and natural gas analysis are declared in table I.

TABLE I
EXPERIMENTAL OPERATING FEED RATIO

| Solid feed | Mass percentage |
|---|---|
| coal | 10% |
| sulfate mixture | 90% |
| gas feed | |
| natural gas | 6% |
| air | 94% |

TABLE II
FEED COMPONENT ANALYSIS

| Coal | | Sulfate mixture | | Natural Gas | |
|---|---|---|---|---|---|
| C | 83% | $Na_2SO_4$ | 85% | $CH_4$ | 85% |
| ash | 13% | NaHSO | 10% | $C_2H_6$ | 8% |
| volatile | 3% | NaCl | 3% | $C_3$ | 3% |
| others | 1% | others | 2% | $N_2$ | 2% |
| | | | | others | 2% |
| total | | | 100% | | 100% |

In table II the analysis of feed component are described. Sulfate mixture are prepared from manheim process is milled up to 15 micrometer average diameter. In order to prevent dust emission during the experiments sulfate powder must be granulated [12] and [6].According to the previous observations which are not concerned in this paper the diffusivity of combusted gas into the core of particles in order to reduction is very slow. On the other hand the residence time of the process gas in the reactor is too short. Due to these restricted limitation, coal up to 10% was used in the feed granulator to increase porosity of granules and make gas penetration easier after coal was converted to gas phase as $CO_2$. This coal is added to feed is named “other source-carbon”.

### *E. Experiments Design*

Feed of reactor were prepared in stated manner which were described before. Data recording started after steady state, when average bed temperature was maintained constant. The feed, product and reactor parameters are summarized in table III.

TABLE III
SUMMARY OF REACTOR PARAMETERS RANGE

| | Parameter | Unit | Range |
|---|---|---|---|
| 1 | residence time | hr | 1.8 ~2.1 |
| 2 | feed density | Kg/lit | 0.9;1.1;1.3 |
| 3 | feed rate | Kg/hr | 528 ~568 |
| 4 | natural gas feed | Kg/hr | 198.9 ~428.9 |
| 5 | air inlet | $Nm^3$/hr | 2400 ~2748 |
| 6 | first bed temperature | ˚C | 968 ~1223 |
| 7 | gas velocity | m/s | 0.78 ~0.8 |
| 8 | CO content in inlet | %w/v | 10 ~11 |
| 9 | CO content in outlet | %w/v | 2.7 ~8 |
| 10 | other source carbon gradient | %w/v | 0.14 ~8.14 |
| 11 | yield of reaction | % | 41.07 ~73 |

Three experiments were carried out. Each experiment lasted eight hours. The density of particles was 0.9, 1.1 and 1.3 in first, second and third experiments, respectively. Gas injection flow rate are adjusted in two level (207 and 345 Kg/hr) and consequently temperature arise to 970˚C and 1220˚C. Fluctuations around this value were occurred due to variation in response of PID controller. Granule carbon gradient percentage in feed and product are measured by definition of insoluble content in feed and product, to reassure these sources of carbon are not reducing agent [13].

### *F. Artificial Neural Network*

Because of ambiguous kinetic of reactions which take place in reactor the ANN methods have been chosen to investigate the dependency of reaction to operating parameters.

ANN is an intelligent method for pattern recognition, which its idea is originated from biological model of the human brain. It consists up of numerous neurons and synapses that large number of simple calculations are carried out through them to reach final target. There are several structures for ANN that Multi-Layer Perceptron (MLP) and Radial Basis Function (RBF) are of the most famous among. Methods to train the synapses of the selected structure, is divided to supervised and unsupervised that supervised methods accept increase of error of estimation during the training process, whereas unsupervised methods do not, which will lead to being trapped in local optimum points. Today, ANNs are vastly used as a powerful tool in estimation, prediction or classification of variables in a multidimensional space [14]-[16]. For a detail study about ANN and its algorithms, respected readers are referred to [17]-[19].

### *G. Multi-layer Perceptron (MLP)*

MLP is the simplest and the most well-known structure among all available structures. It is built up of an input layer, which includes input variables, output layer that contains output variable, and some hidden layers. In this structure, each neuron in each layer is connected by synapses to all the neurons of the next layer that is shown on the fig.2. Each synapse, multiplies the number of previous neuron to its number, and then transforms it to a neuron in the next layer. In hidden layers, each neuron sums input numbers (brought by the synapses), after that, a transfer function is applied on this summation. One of the most well-known and simplest methods for training synapses of MLP networks is backpropagation [18] . In the output layer, usually there is only one neuron that its output is the final goal of classification, estimation or prediction.

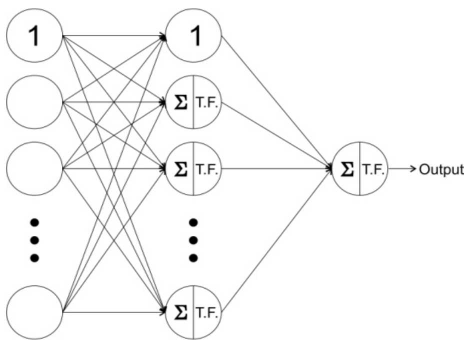



Fig. 2 Illustration of an MLP-structured ANN with one hidden layer (Totally three layers)

## III. RESULTS AND DESCUSION

To estimate Carbon gradient and Yield values, two separate MLP-structured ANNs are trained by backpropagation Levenberg-Marquardt algorithm, which is a supervised method for training MLP networks. Hyperbolic tangent sigmoid was selected as transfer function of all neurons. There were eight input variables that are shown in table IV. Based on small number of available data (96 observations), only one hidden layer with ten neurons is selected to prevent overfitting, furthermore getting closer to a globally acceptable network. 60% of all data is selected randomly as training dataset, 20% for testing the trained network in each epoch of training, and the remaining 20% of original dataset is utilized for checking validation of created network. For each variable, ANN is trained 2000 times and the optimum trained network is selected. Square Root of Mean Squared Error (SRMSE) was the criterion for selecting the most optimum network. SRMSE for the most optimum network of Carbon gradient was 1.00 and 1.54 for Yield. It means that accuracy of estimating these two variables by the created ANNs are 74% and 97% for Carbonate gradient and Yield parameters respectively. Table IV shows brief information of constructed ANNs.

TABLE IV
CHARACTERS AND PARAMETERS OF EACH ANN

| | | Carbon Gradient | Yield |
|---|---|---|---|
| inputs | 1 feed density | ✓ | ✓ |
| | 2 feed rate | ✓ | ✓ |
| | 3 air inlet | ✓ | ✓ |
| | 4 natural gas | ✓ | ✓ |
| | 5 first bed temp | ✓ | ✓ |
| | 6 gas velocity in bed | ✓ | ✓ |
| | 7 CO analysis inlet | ✓ | ✓ |
| | 8 CO in out let | ✓ | ✓ |
| Number of observations | | 96 | 96 |
| Number of hidden layers | | 1 | 1 |
| Number of neurons in hidden layers | | 10 | 10 |
| Training method | | Backpropagation Levenberg-Marquardt | Backpropagation Levenberg-Marquardt |
| Transfer functions | | Hyperbolic tangent sigmoid | Hyperbolic tangent sigmoid |
| Number of iterations | | 2000 | 2000 |
| Mean of output | | 3.85 | 57.58 |
| Square Root of Mean Squared Error (SRMSE) of test data | | 1.00 | 1.54 |
| Precision of Estimation, in percent $\left(1-\frac{Mean\ of\ output}{SRME\ of\ Test}\right)\times 100$ | | 74% | 97% |

For evaluating trained ANNs visually, cross-plots of estimated-actual data are shown in fig. 3 and 4 for other sources Carbon gradient and Yield, respectively. Correlation coefficient of 0.78 in fig3-a indicates that there is no convincing relationship between other source carbon and yield of reaction.

In addition, correlation of 0.84 in fig3-b proves that ANN works properly because test data is assumed as a not-observed dataset. Furthermore, it can be inferred that there is not a relation between Carbon gradient and eight mentioned input variables.

Cross-plots of estimating Yield parameter with correlation coefficients of more than 0.95 in fig4 assures us of the a close relation between yield and input parameters, mentioned in Table IV. Hence, there is a close relation between Carbon gradient and eight mentioned input variables that can be result in estimating Yield with 97% of precision.

## IV. CONCLUSION

This work describes a novel application of natural gas. Experimental study was carried out in fluidized bed reactor with diameter of 115 cm and height of 400 cm. fluidized bed works properly, but some optimization should be considered. Adhesion is the most dominant problem and granules down comer in reactor must be revised. Between temperature range of 968-1200 and about 2 hours residence time, the yield of conversion of sodium sulfate into sodium sulfide is about 57.58%. Negligible difference in initial and final other source carbon content of granules implies that reduction of sulfate is occurred by natural gas.

Theoretical study on data by artificial neural network shows that there is a reasonable rule between the reaction yield and operating conditions. The elevated amount of CO in outlet indicates the need of increasing in height or stages of reactor. More studies must establish to optimize and develop this new kind of natural gas and fluidized bed reactor application.

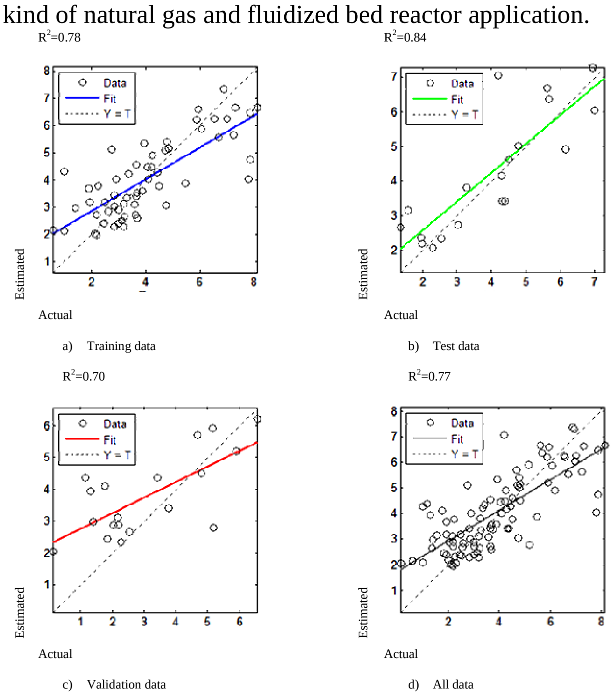
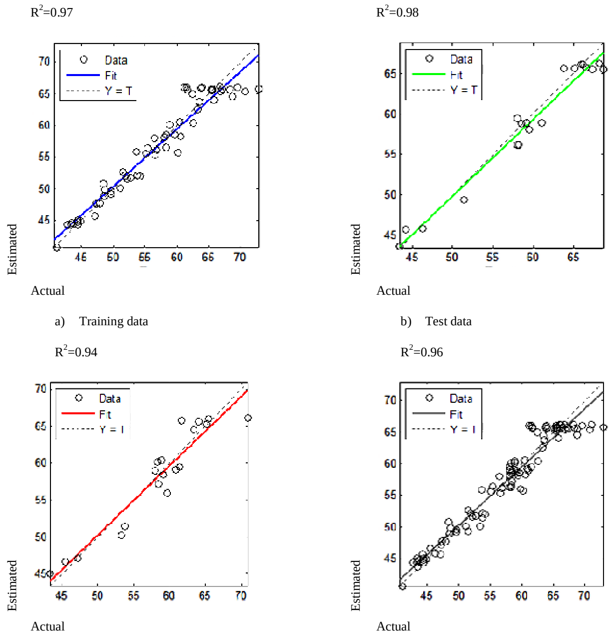



Fig. 3 Carbon gradient estimation by trained ANN




c) Validation data d) All data

Fig. 4 Yield estimation by trained ANN

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