



**INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH  
TECHNOLOGY**  
**THE MODELING OF COBALT CATALYST DEACTIVATION IN THE FISHER-  
TROPSCH SYNTHESIS PROCESS**

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**ABSTRACT**

Cobalt catalyst is one of the most important catalysts that used in the Fisher-Tropsch process. This paper is discussing the deactivating factors of cobalt catalyst. The most important factors can be noted to 4 factors of sintering, coke, poisoning and water. In this study, modeling was conducted in a fixed bed reactor and the corresponding equations were solved using Matlab software. The effect of the temperature and other factors such as the ratio of hydrogen to carbon monoxide was studied on the efficiency and percentage of conversion of components. Data regarding drop of the catalyst activity with time was fitted by a power model and then with respect to the achieved power was discussed about the mechanism of catalyst deactivation. According to the results, the water can be considered one of the most important factors of deactivation of the catalyst.

**KEYWORDS:** activity drop model, cobalt catalyst, Fisher-Tropsch synthesis, deactivation

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**INTRODUCTION**

Fisher-Tropsch process has been found of particular importance in the green industry, transport, fuel and chemical products. Development in the Fischer Tropsch technology requires a full understanding of the reactions, dominant mechanism and kinetics. Although the dominant mechanism has been discussed on the Fischer Tropsch synthesis, but investigations have continued on the common catalysts such as iron and cobalt. With regard to the deactivation of the catalyst is a very big problem in the catalytic processes, understanding the mechanisms of deactivation of the catalyst seems to be essential [1-5]. The purpose of this study is to examine the deactivation mechanism of the cobalt catalyst in the Fischer Tropsch synthesis. Fisher-Tropsch synthesis process is the catalytic process in which liquid hydrocarbons is manufactured from synthesis gas comprising CO and H<sub>2</sub>. None of the previously proposed mechanisms has not generally able to predict the range of observed product for four proposed metal catalysts in the Fisher-Tropsch synthesis namely iron, cobalt, ruthenium and nickel. In addition, the Fischer-Tropsch reaction on the catalysts is lead to produce the range of comparable products together, while the carbide surface is active for iron catalyst. Metal surface is active for cobalt and ruthenium catalyst. Also, the gas-water conversion reaction is raised on the iron catalyst, while this reaction does not take place on the cobalt

or ruthenium catalyst. For mentioned reasons, many researchers assumed that Fischer-Tropsch synthesis mechanism probably is involved more than one of the intermediate key materials [6-9]. They suggested that the mechanism of increasing CO is reason of formation oxygen owners when hydrocarbons are formed to increase CO through the mechanism of free O namely the Caribbean and acids. To insist that many different components contains -C -H and -O has presence on the catalyst surface that may be involved in the Fischer-Tropsch mechanism. So far, studies on the deactivation of catalyst in Fischer Tropsch process were conducted the experimentally in which in a reactor with a specific feed is gained percentage of conversion of substances. parameters can be optimized with regulation of the parameters in equations such as temperature, input feed and so on and so reduce the effect of catalyst deactivation, also, this time model can be included a variety of deactivation mechanisms[10,11]

In this study, reactor and reaction kinetics equations solved in the model with regard to the time relationship of catalyst activity at different times so that the effect of catalyst deactivation is evident on the Fischer-Tropsch.

## FISCHER-TROPSCH PROCESS IN THE PRESENCE OF MODELING COBALT CATALYST

In this study, a fixed bed reactor are modeled with Matlab software with regard to the suitable kinetics of the Fischer Tropsch based on cobalt catalyst and went on to consider the different deactivation models, is examined the effect of catalyst deactivation on the products efficiency and compared the model results with the experimental data and is selected the suitable model of cobalt catalyst activity. For finding the Kinetic model of catalyst deactivation should be determined all chemical and physical processes that lead to the deactivation of catalyst.

### REACTOR MODELING

Equations of the fixed- bed reactor are given with considering the following conditions:

1. Reactor works at steady-state (St. St) conditions.
2. Model is quasi-homogeneous. (it means that there is no concentration and the temperature gradients inside the catalyst particles)
3. There is no temperature gradient and radial concentration inside of the reactor. (namely one-dimensional model for the axis)
4. There is no radial velocity of the gas in the reactor.
5. The radial and axial dispersion have been neglected.

Mass and energy balance equations (quasi-homogeneous model) is the following [12]:

$$-\frac{d(u_s C_i)}{dl} = \rho_p a R_i \quad i=1,2,\dots,NC \quad (1)$$

$$\frac{d(u_s \rho_g C_p T)}{dl} = \rho_p a \sum_{j=1}^{NR} (-\Delta H)_j R_j + \frac{4U}{2R} (T_w - T) \quad j=1,2,\dots,NR \quad (2)$$

To calculate the pressure drop can use the Ergun equation:

$$\frac{dP}{dl} = -(1.75 + 150 \left(\frac{1 - \varepsilon_b}{d_p G / \mu}\right)) \frac{G^2}{1.01325 \cdot 10^6 d_p \rho_g} \left(\frac{1 - \varepsilon_b}{\varepsilon_b^3}\right) \quad (3)$$

Initial conditions for the gas phase can be expressed as the following:

$$l = 0 \rightarrow C_i = C_{i0}, P = P_{in}, T = T_{in} \quad (4)$$

### Reaction kinetics

Following reactions can be noted as main and auxiliary of reaction in the Fischer Tropsch synthesis process.

Table 1 - Main and Auxiliary reactions in the Fisher-Tropsch synthesis

Main reactions	
1.Paraffins	$(2n+1)H_2 + nCO \rightarrow C_n H_{2n+2} + H_2O$
2.Olefins	$2nH_2 + nCO \rightarrow C_n H_{2n} + nH_2O$
3.Alcohols	$2nH_2 + nCO \rightarrow C_n H_{2n+2}O + (n-1)H_2O$
Auxiliary reactions	
4.WGS Reaction	$CO + H_2O \rightarrow CO_2 + H_2$
5. Catalyst Oxidation/Reduction	a) $M_x O_y + yH_2 \rightarrow yH_2O + xM$ b) $M_x O_y + yCO \rightarrow yCO_2 + xM$
6.Bulk Carbide Formation	$yC + xM \rightarrow M_x C_y$
7.Boudward Reaction	$2CO \rightarrow C + CO_2$

### RESULTS AND DISCUSSION

Based on the jess and Kern [12] and the obtained results by them, the concentration profile does not show significant changes in the radial direction of two- dimensional model. Also, the profile of the components concentration, in one and two-dimensional modes has no major changes in comparison with each other. Additionally, the temperature has no significant changes with the reactor length. Therefore, in this study has been considered a quasi-homogeneous one-dimensional isothermal model.

Equation of  $-\frac{d(u_s C_i)}{dl} = \rho_p a R_i$  is showing the Mass

balance for the components existing in the reaction that is the set of ordinary differential equations (ODE), which speed equation is replaced in it. To solve the ODE equations Matlab software has been used. Flowchart of the Matlab program has been given in the following

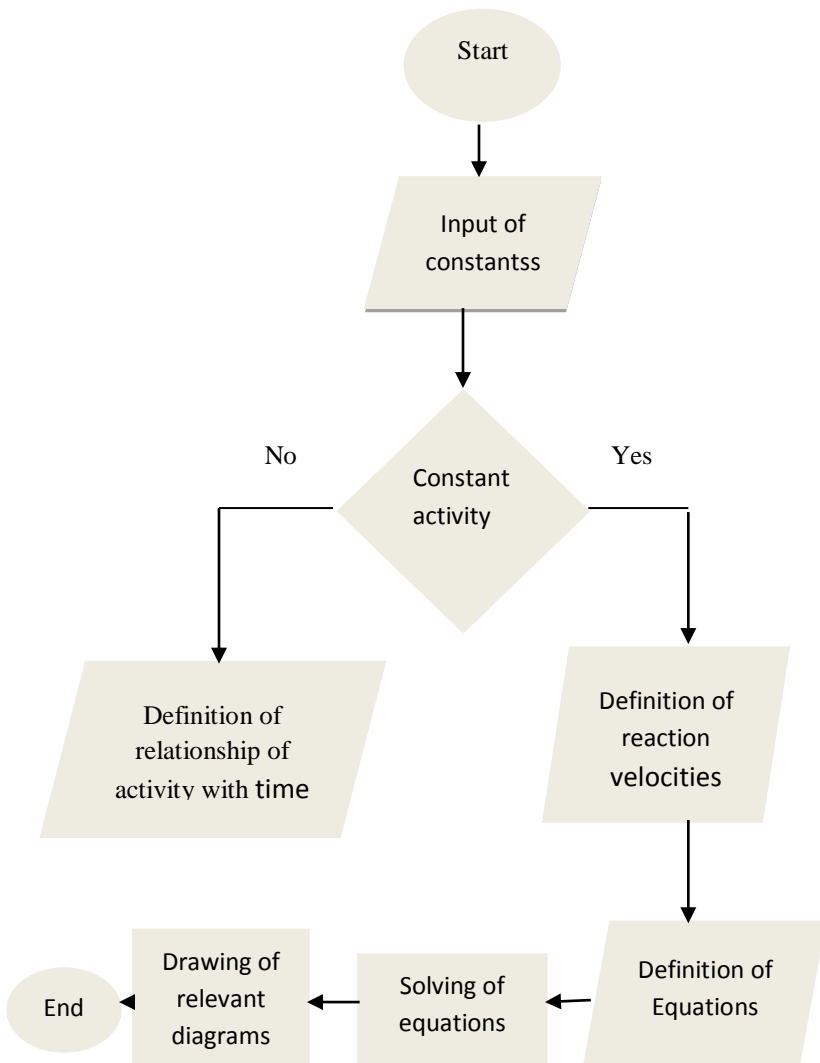


Fig 1. Matlab program flowchart

The information needed to solve the model is presented in Table 2.

Table 2- information for solving the model

$u_s$	0.55 m/s
P	24 bar
$d_p$	3 mm
$\rho_p$	700 kg.m <sup>-3</sup>

Table 3- amount of the conversion of CO at the different given times (model)

Time (hours)	percentage of Co conversion	Time (hours)	percentage of Co conversion
24	87.93	420	84.76
100	87.37	500	84.00
180	86.75	548	83.62
240	86.27	600	83.14
300	85.78	648	82.99
348	85.38	680	82.40
380	85.11	720	82.00

As it is clear from Table 3, the percentage of conversion of CO during a month has decreased from 87.938% to 82% due to the deactivation of the catalyst. In other words, after 30 days the activity of the catalyst reaches approximately up to 93% of its initial value. Same as this study was shown in the Ahmadi Marvast and colleagues' [13] which is given in the Table 4.

Table 4- Values of conversion percentage of CO at different times in Ahmadi Marvast et al study [13].

Day	Time (hr)	Amount of CO conversion	Day	Time (hr)	Amount of CO conversion
1	15	0.87	12	279.5	0.76
2	37.4	0.86	13	302.3	0.74

4	87.9	0.82	15	350.1	0.76
5	107.9	0.83	16	373.6	0.75
6	134.8	0.81	17	401	0.72
8	181	0.78	18	422.3	0.73
9	207.2	0.78	19	450.1	0.72
10	230.5	0.77	20	471.5	0.71
11	253.1	0.74	22	520.4	0.71

Also, in Figures 2 and 3, both of linear and exponential models using the table 4 and Excel software are intended for the drop in activity of the catalyst. The presented Linear model, although despite its simplification can properly meet the need to estimate the amount of catalyst activity after a certain time (in which both of the them are the advantages of above simple and linear models), But does not provide information on the mechanism of deactivation of the catalyst, for this reason another model has been used that with using an exponential equation can correlate the drop data of catalyst activity to the time and also the amount of catalyst activity which exponential equation will be as follows:

$$X = 0.955t^{-0.020} \tag{5}$$

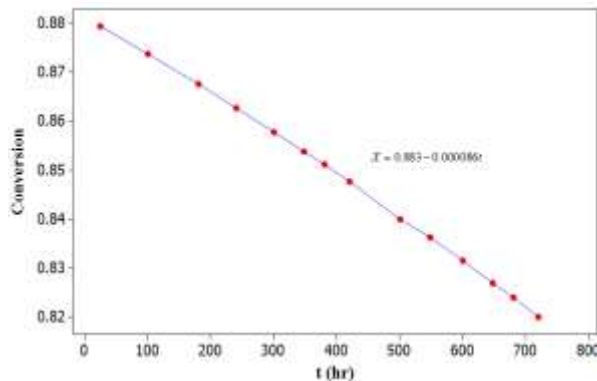
Now, with the Differentiation of this equation based on the time can plot exponential diagram of  $dX / dt$  against X, and then according to achieved power can realize that what is the mechanism of deactivation. The exponential equation is as follows:

$$\frac{dX}{dt} = 0.02 \times X^{-1.021} \tag{6}$$

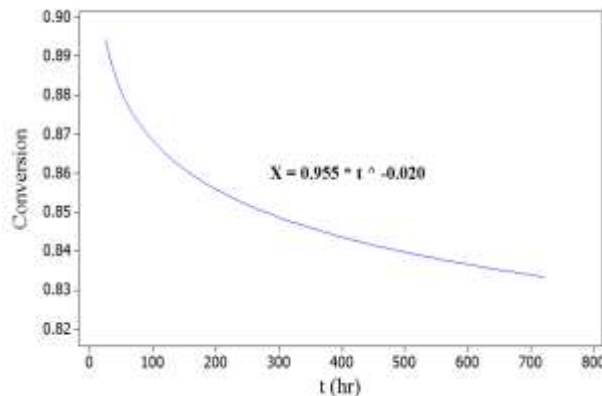
In order to compare the model with other available data, here the results of several similar studies have been brought.

**Table 5- Comparison of drop catalyst activity models in different references**

Referen ce	Linear model of drop catalyst activity	Exponential model of drop catalyst activity
This Work	$X=0.883-0.000086t$	$X=0.955*t^{-0.020}$
14	$X=0.8574-0.0003t$	$X=1.0851*t^{-0.020}$
15	$X=0.7965-0.035t$	$X=0.8568*t^{-0.026}$



**Fig 2. Diagram of percentage drop of conversion vs. time in a linear graph**



**Fig 3. Diagram of activity drop of percentage of conversion vs. time as an exponential graph**

Since the Exponential model is a determiner of the mechanism of drop catalyst activity, according to the table 5, the results of this study are more compatible with the reference number 49 that it is because of most similarity of the assumptions of this research with the cited source.

Mechanisms that may cause the cobalt catalyst deactivation are including: sintering, poisoning, cobalt evaporation, water. In the following, probability of these cases were examined

**CONCLUSION**

This study has been investigated the longevity of cobalt catalyst and the role of various factors in its deactivation. After conducted investigations in the literatures it can be concluded that major factors of deactivation of the catalyst include:

- cobalt oxidation
- migration of cobalt into the base network and the formation of inactive compounds such as aluminate
- The integration and growth of cobalt metal particles on the surface
- Water (cause oxidation of cobalt and base interaction effects and cobalt and the formation of aluminate)
- poisoning by sulfur
- sintering
- coke and carbon precipitation

in order to modeling of Fisher-Tropsch process and predict the kinetics and mechanism of cobalt catalyst deactivation, the equations for the reaction was written based on the fixed bed reactor, then three overall reactions of the Fischer Tropsch process was considered and appropriate kinetic was chosen according to the proposed model. With the help of modeling in the Matlab software, first effects of important parameters on the process were investigated when the activity of the catalyst was constant and equal to one. Modeling results showed that decreasing activity of the catalyst has a significant impact on the distribution of products in the reactor output. This effect can be reduced by choosing appropriate parameters. For the effect of catalyst deactivation, a model for the activity of the catalyst against a time was considered. Then changes of percentage of conversion of CO were obtained with time and eventually a exponential model of time derivation of percent conversion based on percentage of conversion and deactivation equation were obtained as following. With examining each of the inactivating factors, water can be seen as the most important inactivating factors in this field.

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