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Application of Genetic Algorithm in Kinetic Modeling of Fischer-Tropsch Synthesis

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1. Summary

Kinetic modeling is an important issue, whose objective is the accurate determination of the rates of various reactions taking place in a reacting system. This issue is a pivotal element the process design and development particularly for novel processes which are based on reactions taking place between various types of species.
The Fischer Tropsch (FT) reactions have been used as the kinetic modelling bench mark. General kinetic models for FT, Water-Gas-Shift (WGS) and overall rates based on Langmuir-Hinshelwood type have been considered and their optimum parameters have been obtained by Genetic Algorithms. The study shows the obtained model outperforms the other alternative models both in generality and accuracy.
Due to flexibility and generality of Genetic Algorithms, it seems that GA is a useful technique with lots of potentials in determination of optimum kinetic model corresponding to a set of complex reactions.

Keywords: genetic algorithm, kinetic model, optimization, Fischer-Tropsch (FT), water gas shift (WGS).

Extended Abstract:

A general kinetic model is selected by using reasonable reaction mechanisms found in literature. These models are based on Langmuir-Hinshelwood-Hougen-Watson model which can cover most type of FT, WGS and overall syngas rate equations. Most of these equations are presented in Tables 1-3.According to literature, three general models with at least eight unknown parameters were selected as equations 1-3. These models can be used to address various types of kinetic models observed in literatures.

The unknown powers and parameters (decision variables) should be calculated and optimized using GA.

$$r_{FT} = \frac{K P_{CO}^{\alpha} P_{H_2}^{\beta}}{\left(1 + a P_{CO}^{\chi} / P_{H_2}^{\delta} + b P_{H_2O}\right)^{\varepsilon}} \tag{1}$$

$$r_{WGS} = \frac{K(P_{CO} P_{H_2O} / P_{H_2}^{\alpha} - P_{CO_2} P_{H_2}^{\beta} / K_p)}{(\chi + a P_{H_2O} / P_{H_2}^{\delta} + b P_{CO}^{\varepsilon} + c P_{CO_2}^{\phi})^{\varphi}} \tag{2}$$

$$r_{Ovl} = \frac{K P_{H_2}^{\alpha} P_{CO}^{\beta}}{(\chi + a P_{CO}^{\delta} P_{H_2}^{\varepsilon} + b P_{H_2O}^{\phi} + c P_{H_2}^{\varphi} + d P_{CO_2})^{\gamma}} \tag{3}$$

Results and Discussion

To address various proposed FT and WGS kinetic mechanisms a general model was selected with at least eight unknown parameters presented in equations 1-3.
Equations 4-6 represent the optimum models. Table 4 illustrates the performance of the model proposed in this work.

$$r_{FT} = \frac{0.55 P_{CO} P_{H_2}^{1/2}}{1 + 0.65 P_{CO} + 0.6 P_{H_2O}} \tag{4}$$

$$r_{WGS} = \frac{209.218(P_{CO} P_{H_2O} / P_{H_2}^{1/2} - P_{CO_2} P_{H_2} / 66.59)}{\left(1 + 121.02 P_{H_2O} / P_{H_2}^{1/2} + 30.88 P_{CO} + 38.83 P_{CO_2}\right)^2} \tag{5}$$

$$r_{Overall} = \frac{1.92 P_{H_2}^{1/2} P_{CO}^{1/2}}{1 + 2.47 P_{CO} + 173.48 P_{H_2O} + 88.65 P_{H_2}^{1/2} + 164.78 P_{CO_2}} \tag{6}$$

Furthermore, Table 4 shows the comparison of the Absolute Relative Deviations of proposed models in this paper and their best counter parts published by other researchers.

Table 1: Kinetic models of Fischer-Tropsch

Model	*Kinetic Equation*
FT-I	$\frac{kP_{CO}^{1/2}P_{H_2}}{1+aP_{CO}^{1/2}+bP_{H_2O}}$
FT-II	$\frac{kP_{CO}P_{H_2}^{1/2}}{(1+aP_{CO}+bP_{H_2O})^2}$
FT-III	$\frac{kP_{CO}P_{H_2}}{(1+aP_{CO}+bP_{H_2O})^2}$

Table 2: Kinetic models of Water-Gas-Shift

Model	*Kinetic Equation [1-3]*
WGS-I	$\frac{k(P_{CO}P_{H_2O}-P_{CO_2}P_{H_2}^{1/2}/K_p)}{(1+aP_{H_2O}/P_{H_2}^{1/2})^2}$
WGS -II	$\frac{k(P_{CO}P_{H_2O}-P_{CO_2}P_{H_2}/K_p)}{P_{CO}P_{H_2}+aP_{H_2O}}$
WGS -III	$\frac{k(P_{CO}P_{H_2O}-P_{CO_2}P_{H_2}/K_p)}{P_{CO}+aP_{H_2O}+bP_{CO_2}}$

Table 3: Kinetic models of Overall syngas consumption

Model	*Kinetic Equation [1-3]*
OVL -I	$r_{Overall}=\frac{KP_{H_2}^{1/2}P_{CO}^{1/2}}{(1+aP_{CO}^{1/2}+bP_{H_2}^{1/2})^2}$
OVL -II	$r_{Overall}=\frac{KP_{H_2}^{1/2}P_{CO}}{(1+aP_{CO}+bP_{H_2}^{1/2})^2}$
OVL -III	$r_{Overall}=\frac{KP_{H_2}P_{CO}}{(1+aP_{CO})^2}$

Conclusion

Unlike traditional gradient based methods one of the most important characteristic of Evolutionary Algorithms such as GA is their effectiveness and robustness when they are used to optimize the problems which inherently uncertain and/or ill-defined. In this approach minimum human effort and little insight into the details of the chemical mechanism are required to obtain the optimum value for the reaction rate parameters.

Despite the flexibility and robustness of GA, its efficiency heavily depends on the type of genetic operators used in the algorithm and their corresponding parameters. In this study the appropriate type of genetic operators and their parameters have been studied and obtained.

Due to flexibility and generality of Genetic Algorithms, it seems that GA is a useful technique with lots of potentials in determination of optimum kinetic models corresponding to a set of complex reactions.

Table 4: Results of this study and comparison with other results

Model	***Average Percent Relative Error***	***Model***	***Average Percent Relative Error***	***Model***	***Average Percent Relative Error***
4	*27.78186*	***5***	*27.61686*	***6***	*26.60664*
FT-I	*42.89747*	***WGS-I***	*86.82425*		
FT-II	*54.49429*	***WGS-II***	*84.88095*		
FT-III	*54.93696*				

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