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Numerical methods for reaction kinetics parameters: identification of low-temperature propane conversion in the presence of methane

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Abstract

Numerical methods for reaction kinetics parameters identification for low-temperature steam propane conversion (LTSC) of associated petroleum gas (APG) are described based on an example of the methane-propane mixture. LTSC reaction of light hydrocarbons on nickel catalysts allows us to considerably improve fuel characteristics of the APG. Reactants concentrations along the length of the reactor for various temperatures are obtained. The solution to the inverse kinetic task allows us to define optimum kinetic parameters of the reaction.

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Keywords: mathematical modeling; chemical kinetics; associated petroleum gas; low temperature steam conversion; catalysis; Jacobian matrix; Rosenbrock's method; high-dimensional optimization; direct search method

1. Introduction

The need of low cost hydrocarbon fuels, as alternatives to oil, is well known. One of such fuels is the associated petroleum gas (APG). APG is the multicomponent gas mixture produced from oil during primary separation. APG is potential raw material for valuable chemical products, such as fluid organic compounds. This gas, however, needs to be separated correctly from oil in order to meet the required standards.

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There are many technologies of APG utilization [1, 2]. One of methods is to use of APG immediately on the oil fields.

This method, however, is suitable only for those gases, the transportation of which to gas processing equipment and refineries is unprofitable. These gases include stabilization gas and associated petroleum gas from hard-to-reach and low-pressure fields. Such gases are typically burnt in torches. It is primarily related to poor infrastructure development. There are no economically viable technologies of utilization of APG in the locations of oil production in most cases. One of the alternate methods applicable to large-scale deposits is the low-temperature steam conversion (LTSC) of light hydrocarbons [3, 4, 5].

The purpose of this work is determination of the kinetic parameters (pre-exponential factors and activation energies) for the mathematical model describing this process based on the solution to the inverse problem of chemical kinetics using the experimental data.

2. Numerical Methods

2.1. Direct Problem of Chemical Kinetics

To describe the process of propane low-temperature conversion, the two-stage macro-kinetic model of the process was suggested. The first stage of the process is the steam conversion of propane, and the second one represents a reversible methanation reaction of carbon dioxide [5]:

$$CO_2 + 4H_2 = CH_4 + 2H_2O, \tag{1}$$

$$C_3H_8 + 6H_2O = 10H_2 + 3CO_2. \tag{2}$$

The following notations are used:
X_1 – concentration of propane (C_3H_8), *[mol/m^3]*;
X_2 – concentration of water (H_2O), *[mol/m^3]*;
X_3 – concentration of a carbon dioxide (CO_2), *[mol/m^3]*;
X_4 – concentration of hydrogen (H_2), *[mol/m^3]*;
X_5 – concentration of methane, *[mol/m^3]*.
The following expressions is used to describe the temperature dependence of the reaction rates [3, 4, 5]:

$$W_1 = k_1 e^{\frac{-E_1}{R*T}} X_1, \tag{3}$$

$$W_2 = k_2 e^{\frac{-E_2}{R*T}} X_4 \left[1 - \frac{P_{CH_4} P_{H_2O}^2}{K_{eq} P_{CO_2} P_{H_2}^4} \right], \tag{4}$$

where
W_1, W_2 – reaction rates, *[mol/(s·m^3)]*;
$k_1=10^{10.9}$, $k_1=10^{5.8}$ – pre-exponential factors of reactions, *[s^{-1}]*;
$E_1=112$, $E_2=50$ – activation energies of reactions, *[kJ/mol]* [2];
$R = 8.31$ – universal gas constant, *[kJ/ (mol·K)]*;
X_1, X_4 – propane and hydrogen concentrations, *[mol/m^3]*;
P_i – partial pressure of the *i*th gas component, *[bar]*;
K_{eq} – thermodynamic equilibrium constant of CO_2 methanation (reaction (2)), *[bar^{-2}]*, the value is calculated from [6].
The material balance equation for LTSC is presented as [5, 7]: