

Synthesis gas conversion into hydrocarbons (gasoline range) over bifunctional zeolite-containing catalyst: experimental study and mathematical modelling

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Abstract

Bifunctional catalysts were investigated in the temperature range 320–400 °C, at pressures 40–80 atm, GHSV = 500–20,000 h⁻¹, ratio H₂/CO = 2–10. The influence of the Zn–Cr/ZSM-5 catalyst composition on the products distribution and the process productivity with regard to the liquid hydrocarbons (gasoline range) has been studied. It has been shown that the products distribution depends mainly upon the molar ratio H₂/CO and GHSV, while the main factors affecting the process productivity and the yield of the liquid hydrocarbons are pressure and temperature in the reactor.

On the basis of the experimental data, mathematical modelling has been performed for the process flow sheet with the unreacted gas recycled. The influence of various parameters of the process on the catalyst productivity with regard to liquid hydrocarbons was studied.

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Keywords: Synthesis gas conversion; Bifunctional catalysts; Mathematical modelling; Liquid hydrocarbons

1. Introduction

The transformation of synthesis gas into liquid hydrocarbons attracts significant attention as an alternative way for motor fuels production. During the recent decades, a great number of scientific, pilot and industrial investigations have been made for different versions of the process of natural gas conversion to gasoline via synthesis gas. Three versions of synthesis gas transformation to gasoline are schematically illustrated in Fig. 1.

Many investigations have demonstrated the advantages of the one-stage processes using bifunctional catalysts (version c) compared with the two-stage and three-stage processes of synthesis gas conversion to gasoline [1–3].

The bifunctional catalysts for the transformation of synthesis gas to liquid hydrocarbons, composed of metallic oxides (ZnO–Cr₂O₃) and ZSM-5 zeolite, have been proposed by Chang [4,5]. The overall chemical reaction was the

following: (i) the conversion of synthesis gas to methanol, then (ii) the subsequent conversion of methanol to gasoline on ZSM-5 and finally (iii) the CO₂ formation by water-gas-shift reaction. Chang et al. have reported that by using the bifunctional catalysts, the hydrocarbons of gasoline range can be effectively formed from synthesis gas at 427 °C under 83 atm. In [1] this reaction is studied in detail using the said catalyst under mild conditions (264–344 °C and 10–45 atm). It was shown that the maximum selectivity towards aromatic hydrocarbons can be obtained at 284 °C under 40 atm.

Many investigations are focused on studying the kinetic regularities of methanol conversion into hydrocarbons [6–10]. One of the first models has been proposed by Chang [5]. The model satisfactorily describes the reaction products distribution as regards paraffins, aromatics, olefins and oxygenates in the temperature range 302–370 °C within a wide range of conversions. In [7], three lumped kinetic models were developed and tested for the same temperature range, describing ethylene, propylene, butylenes and paraffins forming from oxygenates (methanol and DME). Michail et al. performed a detailed analysis of the possible reactions (about 53

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Nomenclature

\bar{c}_p	heat capacity of the mixture (kcal kg ⁻¹ K ⁻¹)
C_i	the molar fraction of the <i>i</i> th component
F_i	rate of change for the <i>i</i> th reagent
ΔH_i	change in the reaction enthalpy (kcal mol ⁻¹)
k_i	reaction rates constants (s ⁻¹)
K_i	equilibrium constants
l	the bed height coordinate (m)
N_c	mole ratio the recycle gas (V_s) to the feed gas
P	total pressure (atm)
P_i	partial pressure of reagents (atm)
u	superficial velocity along the reactor (m s ⁻¹)
V_i^b	bypass gas flow at the <i>i</i> th catalyst bed inlet (m ³ s ⁻¹)
V_s	(= $V_1 + \sum V_i^b$) total gas flow (m ³ s ⁻¹)
V_1	gas flow at the first catalyst bed inlet (m ³ s ⁻¹)
W_i	rate of <i>i</i> th reaction (s ⁻¹)

Greek symbols

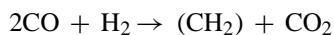
α	coefficient of change of the volumetric flow during the chemical reactions
ξ	dimensionless coordinate of the beds height
ρ	bulk density (kg m ⁻³)

Indices

in	inlet
out	outlet

reactions) and obtained kinetic parameters [8]. However, the great number of kinetic constants makes it difficult to use the kinetic model in practical mathematical modelling.

In further studies [9] another technique was used for modelling hydrocarbon synthesis from synthesis gas over bifunctional catalysts. Only the following overall reaction of CO conversion to hydrocarbons was taken into account:



The reaction rate equation has been evolved by modification of the kinetic equation for methanol synthesis under the assumption that the water-gas-shift reaction was fast and the overall rate of synthesis gas conversion into hydrocarbons was limited by the methanol formation stage.

Several available kinetic models for methanol synthesis were modified in a similar way to describe liquid hydrocarbons production directly from syngas [10]. These modified models involve a rate equation with a CO₂ concentration-dependent term.

The effectiveness of liquid hydrocarbons production from synthesis gas depends on a great number of technological parameters such as the feeding gas composition, the temperature in the reactor, the circulation rate (the molar ratio of recycle and feeding gases), the contact time of the reaction mixture

with catalyst etc. All these parameters are interrelated so that changing one of them causes changes in the others. It changes the reactor productivity as well as the overall conversion of the carbon contained in the feed synthesis gas to the target products, thus affecting the economical indices of the process as a whole.

The main point of this paper is experimental and theoretical studying the effect of technological parameters of the process on the catalyst selectivity and productivity with regard to liquid hydrocarbons.

2. Experimental

ZSM-5 type zeolite was prepared by hydrothermal synthesis. To prepare bifunctional catalysts, powders of ZSM-5 zeolite component and ZnO–Cr₂O₃ component, in the desired proportion, were homogenized in a mortar with further pressing, crushing and sieving. The particle fractions of 0.25–0.5 and 3–4 mm were used in the reaction.

In the present work, we have catalytically examined the one-stage synthesis gas conversion to hydrocarbons (version 3) in a fixed bed flow reactor. The experimental setup includes the following units: a single-tube reactor (length 0.5 m, ID 0.01 m), a high-pressure separator, a low-pressure vessel (tank) and a circulation compressor. To provide isothermal catalyst bed, the reactor was placed into a furnace with fluidised sand. The gas flow from reactor was cooled to 20 °C and sent in a high-pressure separator to fractionate liquid reaction products – gasoline, water and methanol. Gaseous reaction products and unconverted syngas were passed through analysers. If needed, the gas leaving the high-pressure separator was fed back in the reactor by means of circulation compressor. Periodically, the separated liquid fractions were fed into a low-pressure vessel (tank) to remove the major part of dissolved gaseous reaction products – C₂–C₅ hydrocarbons, CO₂ and dimethyl ether (DME). Methanol, DME and water were analysed with a TCD using a column filled with chromosorb-102. The gaseous hydrocarbons were analysed with a TCD using a column packed with Al₂O₃. The liquid hydrocarbons were analysed by the TCD using a 3-m long column with Benton-34/SP-1200 on 100/120 Supelcoport or by the flame ionisation detector (FID) with a 50-m long capillary column. The identification of products was performed by GC–MS.

For the bifunctional catalyst used in the studied process, the balance between its hydrogenating and acidic functions is its important characteristic. That is, the catalyst should provide the maximum conversion of methanol, primarily formed from syngas on hydrogenating sites, into final liquid hydrocarbons (on acidic sites). This characteristic of bifunctional catalyst can be controlled through adjusting the ratio of its hydrogenating and acidic components. For a bifunctional catalyst, there exists no universal component ratio. The substitution of a highly acidic component by a component showing lower acidity should be accompanied by

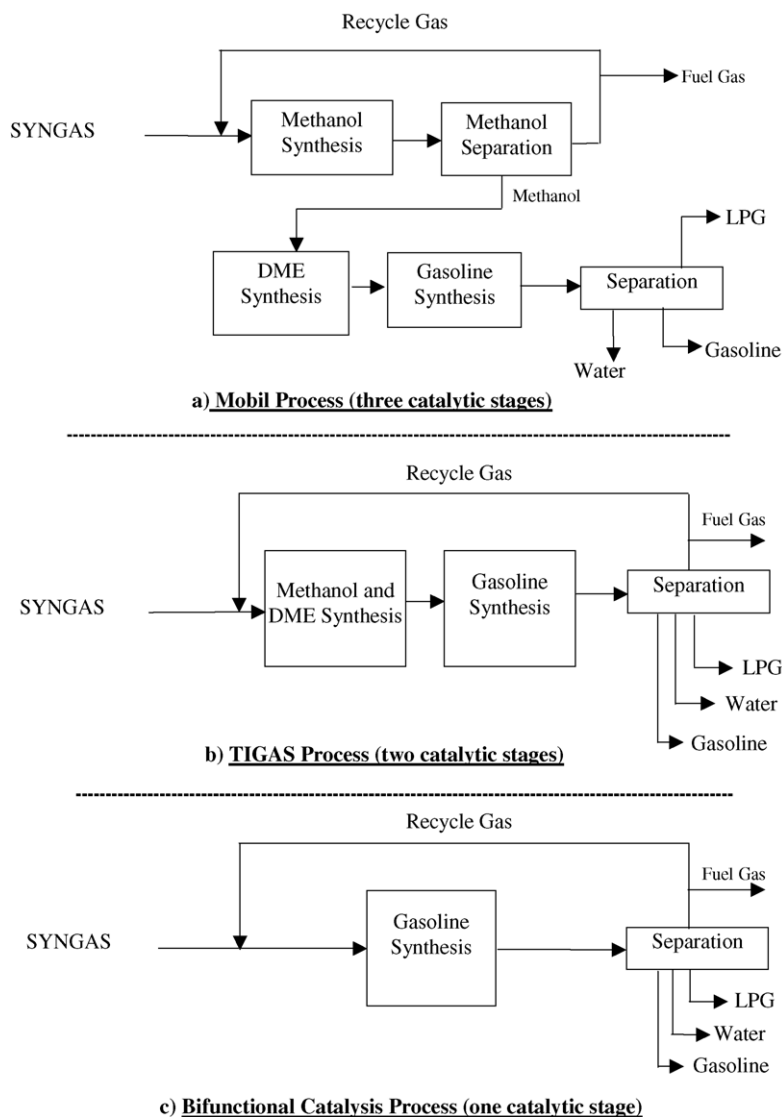
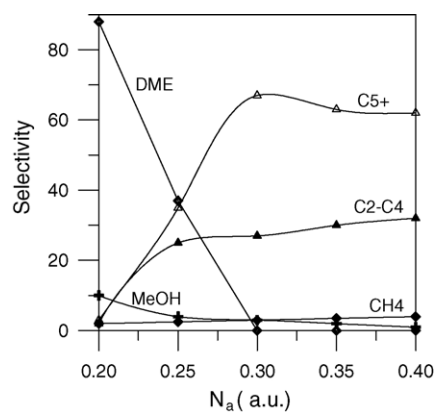


Fig. 1. Different types of gasoline synthesis processes.

the increase of specific fraction of the acidic component in the catalyst composition. Otherwise, the catalyst functional balance will be disturbed. In order to characterize the balance of catalytic functions in bifunctional catalysts, the factor of relative acidity (N_a) has been introduced. Fig. 2 illustrates how the process selectivity changes with changing relative acidity of a bifunctional catalyst. In the case of low relative acidity ($N_a < 0.25$), the process is limited by the stage of DME dehydration to ethylene, while in the case of high acidity ($N_a > 0.35$) the catalyst selectivity toward C_{5+} -hydrocarbons decreases due to intensification of cracking of aliphatic hydrocarbons to C_2 – C_4 hydrocarbons. As Fig. 2 shows, the maximum selectivity of the given bifunctional catalyst towards gasoline fraction (C_{5+}) is attained at $N_a = 0.3$.

As the hydrocarbon synthesis proceeds, the coking of the acidic component inevitably occurs, which decreases the total acidity of bifunctional catalyst. Finally, as N_a attains the minimum permissible value, the functional balance breaks and

Fig. 2. Effect of the bifunctional catalyst acidity N_a (relative units) on the process selectivity. $P = 80$ atm, $T = 380$ °C.

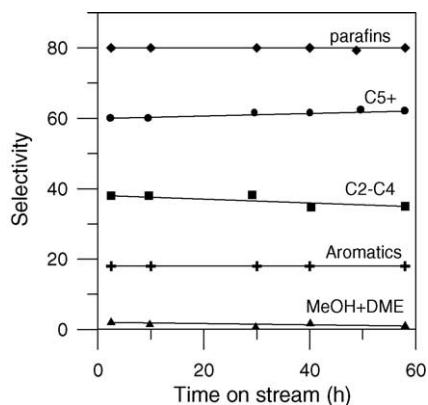


Fig. 3. Organic products distribution as function of time-on-stream. $P=80$ atm, $T=380$ °C, $\text{GHSV}=4000$ h^{-1} , $\text{H}_2/\text{CO}=2.3$.

catalyst's selectivity changes. Therefore, to perform kinetic experiments, one should determine the period of the stable catalyst operation. As can be seen in Fig. 3, the studied bifunctional catalyst showed a 60-h stable operation in the synthesis of liquid hydrocarbons from syngas. Based on the obtained stability data, the kinetic experiments were performed with the periods of continuous catalyst operation 10–170 h.

It has already been shown how pressure and temperature affect the productivity toward C_{5+} in the synthesis of hydrocarbons from CO and H_2 over the studied bifunctional catalytic systems [11]. We reported that in pressure and temperature intervals of 40–80 atm and 320–400 °C, respectively, the maximum conversion falls at the upper limits of these parameters (80 atm and 400 °C). Since the studied bifunctional catalyst had demonstrated stable operation in a flow reactor at a pressure of 80 atm and temperature 380 °C, the further experiments were performed under these conditions.

Fig. 4 represents the dependence of catalyst selectivity toward C_{5+} and oxygenated products (methanol and DME) in synthesis from syngas on space velocity. Methanol and

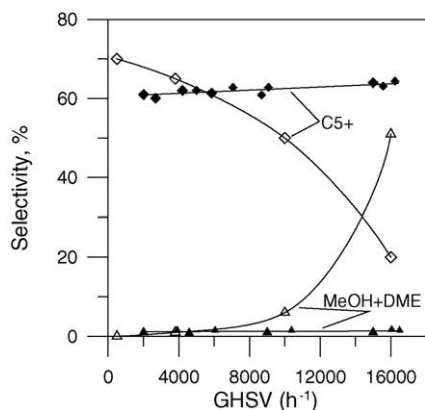


Fig. 4. Concentrations of C_{5+} and methanol + DME in organic products depending upon GHSV at various acidities N_a (relative units) of bifunctional catalysts. $P=80$ atm, $T=380$ °C, $\text{H}_2/\text{CO}=2.3$. Light symbols: $N_a < 0.3$, dark symbols: $N_a > 0.3$.

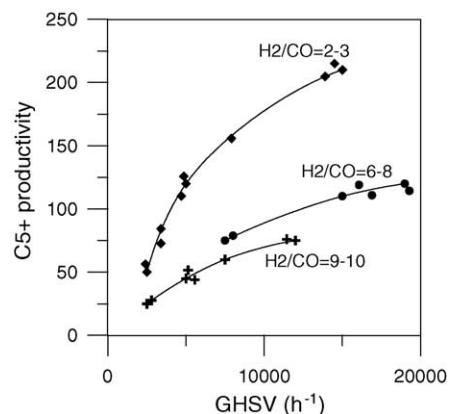


Fig. 5. Dependence of C_{5+} productivity ($\text{g}/\text{catalyst}/\text{h}$) on GHSV. $P=80$ atm, $T=380$ °C.

DME are intermediate products of syngas conversion to hydrocarbons. With the catalyst of the increased acidic function ($N_a > 0.3$), their content in final reaction products is two orders of magnitude lower than the content of gasoline hydrocarbons. High concentration of methanol and DME in products mixture indicates the decrease of the catalyst acidic function. Such violations of catalyst's functional balance, resulting from the deactivation of acidic component or wrong components ratio, first of all appear at high space velocities of syngas. Fig. 4 shows how the selectivity of the process proceeding on the catalyst with decreased acidic function ($N_a < 0.3$) changes depending on varying syngas space velocity. At $\text{GHSV} < 4000$ h^{-1} , the increase of space velocity causes a slight decrease in selectivity to C_{5+} and an insignificant increase of methanol and DME content in the reaction products. As syngas space velocity increases to 16,000 h^{-1} , the process selectivity to C_{5+} falls to 20 wt.% and methanol and DME constitute a half of reaction products.

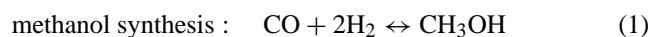
Earlier we have studied the effect of molar ratio H_2/CO on syngas conversion to C_{5+} hydrocarbons in the flow-circulation reactor [11]. It has been shown that the increase of H_2/CO molar ratio from 0.6 to 2.8 causes the decrease of the content of aromatics in C_{5+} hydrocarbons from 80 to 23 wt.%. In the present work we have studied how molar ratio H_2/CO in the reactor input affects the process selectivity under flow conditions. The results are presented in Fig. 5. It is seen that as the syngas space velocity increases, the conversion toward C_{5+} hydrocarbons grows, while the intensity of conversion growth decreases following the increase of molar ratio H_2/CO in the reactor input.

3. Kinetic model

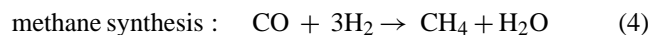
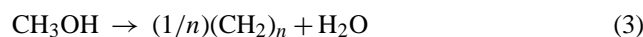
It is known that to model the process of hydrocarbon production, it is necessary to use not only a mathematical model but also the kinetic equations describing the regularities of reagents changes during chemical reactions.

As regards the process of synthesis gas conversion into hydrocarbons over bifunctional catalysts, it includes a set of different reactions involving a great number of reagents and is therefore one of the processes most difficult for analysis. Over a bifunctional catalyst, methanol and hydrocarbons are simultaneously formed out of CO/H₂/CO₂ mixture in contrast to the like processes with an intermediate stage of methanol isolation. It is thermodynamically preferable to realize the reaction of hydrocarbon synthesis directly from syngas in a single reactor without the intermediate methanol isolation. It allows shifting the equilibrium of the reversible reaction of methanol synthesis. The methanol synthesis and the water-gas-shift reaction proceed over the methanol synthesis catalyst component while the further methanol conversion into hydrocarbons proceeds over the zeolite component.

The following overall reactions play a role:



hydrocarbons synthesis (gasoline range) :



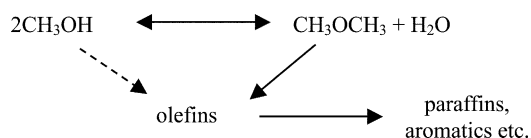
The reaction of methanol synthesis is rather well studied. There are kinetic equations in good agreement with the experimental data for different catalysts. To construct a model, we used the kinetic equation of the methanol synthesis reaction over Cr₂O₃–ZnO catalyst, which in our case was a part of bifunctional catalyst [12]:

$$W_1 = k_1 \left(P_{\text{H}_2} \frac{P_{\text{CO}}^{0.25}}{P_{\text{CH}_3\text{OH}}^{0.25}} - \frac{P_{\text{CH}_3\text{OH}}^{0.25}}{P_{\text{CO}}^{0.25} K_1} \right) \quad (5)$$

Water-gas-shift reaction at temperatures $T > 300$ °C was supposed fast and calculated by the following equation:

$$W_2 = k_2(P_{\text{CO}_2}P_{\text{H}_2} - P_{\text{CO}}P_{\text{H}_2\text{O}}K_2^{-1}) \quad (6)$$

It is known that olefins are formed from dimethyl ether [13]. However as the dimethyl ether concentration is very small, for the modelling it is convenient to use the Chang scheme of hydrocarbon formation modified by Voltz and Wise [4]:



According to this reaction scheme, the rate of the hydrocarbon formation can be described, in the simplest case, by the following equation:

$$W_3 = k_3 P_{\text{CH}_3\text{OH}} + k_3'' P_{\text{DME}}$$

Taking into account the fact that, according to the above scheme, the rate of dimethyl ether formation is in proportion to methanol concentration and in inverse proportion to water concentration, the following kinetic equation is obtained:

$$W_3 = P_{\text{CH}_3\text{OH}} \left(k_3 + \frac{k_3' P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2\text{O}}} \right) \quad (7)$$

The rates of methane formation were calculated by using the following first-order equations with respect to carbon monoxide partial pressure:

$$W_4 = k_4 P_{\text{CO}} \quad (8)$$

The rate constants and activation energies of the Eqs. (5)–(8) were determined on the basis of the experimental data obtained for an isothermal flow reactor and a two-bed adiabatic reactor [6].

4. Mathematical model

The main unit of a chemical-technological scheme is a reactor, its choice being determined by both technological and economical criteria. Taking into consideration the kinetic regularities of the process, rather high heat of reactions and the limit of thermal stability of the catalyst, those reactors which are capable of supporting the operational conditions in a sufficiently narrow temperature range are preferred.

These are, first of all, fluidised bed reactors and multi-tube reactors. Each of them has its advantages and disadvantages. The advantages of a fluidised bed reactor are as follows: its technological arrangement is simple; catalyst particles are easy to inject and remove while changing catalyst; it is possible to maintain the isothermal mode of the reactor operation. An essential disadvantage is that this kind of reactor requires high mechanical strength and low attrition of the catalyst particles. Multi-tube reactors allow maintaining nearly isothermal conditions but they are too cumbersome for installations of high capacity.

The processes of hydrocarbon production from methanol (MTG) and directly from synthesis gas (TIGAS) have been experimentally examined for various types of reactors including fluidised bed reactor [14], pseudoadiabatic fixed-bed reactor [2,9], monolithic reactor with parallel tubes with catalytic material deposited in the walls [15]. One of the main advantages of catalytic monolithic reactors is a very low pressure drop.

In the present paper, the fixed multi-bed reactor is chosen. To model the process of hydrocarbon synthesis in a fixed bed reactor, a plug flow model taking account of the gas volumetric flow changing in the course of the reaction was developed. The mass-and-heat balance equations can be written as

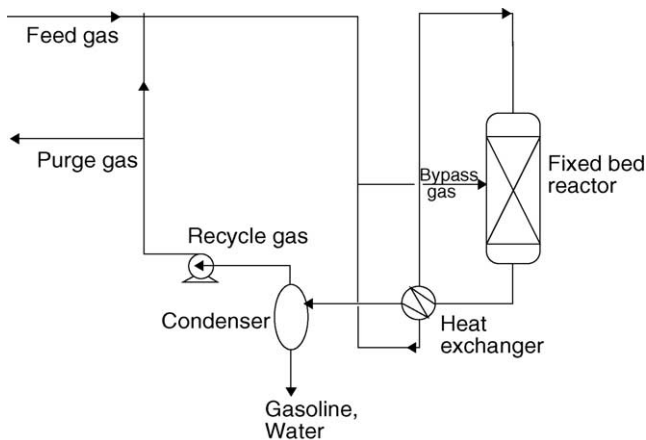


Fig. 6. Simplified flow diagram of syngas conversion to gasoline.

follows:

$$\frac{dC_i}{dl} = \frac{1}{u} \left(F_i - \sum_k F_k \right), \quad \frac{du}{dl} = \sum_k F_k,$$

$$\bar{c}_p \bar{\rho} u \frac{dT}{dl} = \sum_j (-\Delta H_j W_j) \quad (9)$$

with boundary conditions: $l=0, C_i=C_i^0, T=T^0, u=u^0$.

The flow diagram of syngas conversion to hydrocarbons is shown in Fig. 6. After being mixed with the recycle gas and heated up in the heat exchanger up to the initial reaction temperature, the synthesis gas is fed to the reactor inlet. From the reactor, the hot gas passes through the heat exchanger where it is partially cooled by the cold reaction stream. After that, while passing the separator, the stream is separated into the liquid fraction and the gaseous fraction to be recycled. To prevent accumulation of the inert in the recycle gas, either being added from the feed gas (N_2, CH_4) or being formed in the reaction course (light hydrocarbons), part of the recycle stream is removed out of recycle loop as a purge gas. Stream cooling between the beds of the reactor is carried out via bypass of part of the recycle gas.

The mathematical model simulating the technological scheme with recycle involves both differential and algebraic equations describing separate units and connections between them. There are various techniques for solving the like problems but all of them include a common calculation algorithm. In our case, the calculation sequence was as follows:

- The values of temperature, concentrations and superficial velocity at the reactor inlet were assigned as the initial approximation.
- By the reactor modelling, the concentrations of the reagents at the reactor outlet were determined.
- The liquid fraction including water, methanol and hydrocarbons formed through the reactions was separated out of the system while the remaining stream was recycled.
- Part of the recycle stream was purged off and the remaining part was mixed with the initial synthesis gas.

Thus, the problem of finding a steady-state solution for the mathematical model of technological scheme with recycle loop can be essentially reduced to solving the nonlinear system of the form:

$$\vec{C} = \Psi(\vec{C})$$

The conventionally used methods for solving such problems are the simple iteration method, Newton's method or one of the gradient methods of discrepancy functional minimization.

5. Results and discussion

The effectiveness of liquid hydrocarbons production from synthesis gas depends on a great number of technological parameters such as the feeding gas composition, the temperature in the reactor, the circulation flow rate, the volume of the purge gas, the contact time of the reaction mixture, the separator temperature, etc. All these parameters are interrelated so that changes in one of them causes changes in the others. It results in a change in the productivity of 1 m^3 of the catalyst as well as in the overall conversion of the carbon contained in the feed synthesis gas.

One of the main parameters affecting the carbon conversion to target products is the ratio of the purge gas to the feeding gas. On one hand, increasing this parameter causes a more reactive mixture to be established at the recycle thus increasing the productivity of 1 m^3 of the catalyst; on the other hand, an increase in the purge gases volume decreases the degree of carbon conversion to the hydrocarbons.

So the calculations have been performed to define the influence of the volume of gases purged out of recycle on catalyst productivity for various gas GHSV values. The results are shown in Fig. 7. As a feeding gas, syngas of the following composition was taken: $CO = 23.937\%$, $H_2 = 67.089\%$, $CO_2 = 8.035\%$, $CH_4 = 0.4301\%$, $N_2 = 0.4686\%$.

The reactor productivity depends on the gas composition at the reactor inlet. For the recycling scheme, the light hydrocarbons are accumulated as well as hydrogen and the inert

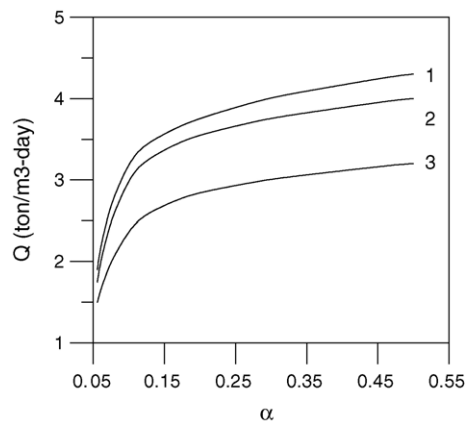


Fig. 7. Dependence of the 1 m^3 catalyst productivity (Q) vs. the fuel gas/feed ratio (α) at: GHSV = $23,000 \text{ h}^{-1}$ (curve 1), $18,000 \text{ h}^{-1}$ (2), $9,000 \text{ h}^{-1}$ (3).

gases contained in the feed gas. The concentration of hydrogen at the recycle depends on how much the $\text{CO}/\text{H}_2/\text{CO}_2$ mixture deviates from the stoichiometric composition for the reaction, the latter being defined by the so-called module $f = (\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$ [16]. The module value close to 2.0 corresponds to the stoichiometric composition for the reaction of syngas conversion into hydrocarbons, $f < 2$ corresponds to hydrogen deficiency, and with $f > 2$, hydrogen is getting accumulated at the recycle. An increase in the hydrogen partial pressure is known to decrease catalyst deactivation rate, however large accumulation of hydrogen would decrease the hydrocarbon formation reaction rate.

In Fig. 7, the dependence of the catalyst productivity per volume unit versus the parameter α is shown. The figure demonstrates the productivity decrease with decreasing the purge gas volume. The decrease is especially sharp for $\alpha < 0.1$. It is caused both by decrease in the quantity of the gasoline range hydrocarbons being formed and by accumulation of essential amounts of the carbon-containing components as well as of inert gases ($\text{CH}_4 + \text{N}_2$) contained in the initial gas. As a result, lesser and lesser amounts of the feeding gas to maintain the fixed pressure ($P = \text{const}$) are fed to the recycle. It should be noted that increasing the purge gases volume increases productivity of the catalyst volume unit but decreases the conversion degree for carbon contained in the feeding gas to hydrocarbons. For example, for $\alpha = 0.05$ conversion degree of carbon is 90–92% while for $\alpha = 0.3$ the value is 68–70%.

The reaction of synthesis gas conversion into hydrocarbons is highly exothermic: at the temperature of 380 °C the reaction heat is comprised of 750 kcal/kg of methanol at the stage of its forming and 450–500 kcal/kg at the stage of its conversion. So increase in the GHSV not only increases catalyst productivity (Fig. 7) but also decreases the overall heat of reactions (Fig. 8). It allows lessening the number of catalyst beds.

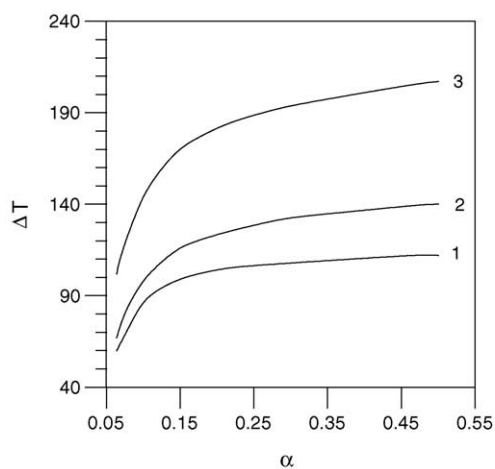


Fig. 8. Dependence of the temperature increment in the catalytic reactor vs. the fuel gas/feed ratio (α) at: GHSV = 23,000 h^{-1} (curve 1), 18,000 h^{-1} (2), 9000 h^{-1} (3).

For a 4-bed reactor with gas stream cooled down between the beds via a bypass, the catalyst loading distribution by the catalyst beds looks as follows (relative units): 1st bed – 0.22, 2nd bed – 0.24, 3rd bed – 0.26, 4th bed – 0.28. Catalyst volume for each bed is calculated for the temperature conditions $T^{\text{in}} = 360$ °C, $T^{\text{out}} = 390$ °C. The increase of catalyst volume with the number of the catalyst bed is mainly due to the gas stream increase caused by adding bypass gas. The gas volume fed to the 1st catalyst bed V_1 and the volume of the bypass gas V_i needed to cool down the inlet gas stream for the i th bed of an n -bed reactor can be estimated, in the simplest case, by the following relation:

$$V_i^{\text{b}} = V_1 \alpha \beta q^{i-2}, \quad i = 2, \dots, n$$

where

$$\beta = \frac{\bar{c}_p^{\text{out}} T^{\text{out}} - \bar{c}_p^{\text{in}} T^{\text{in}}}{\bar{c}_p^{\text{in}} T^{\text{in}} - \bar{c}_p^{\text{b}} T^{\text{b}}},$$

$$V_1 = \frac{V_s}{1 + \alpha \beta (1 - q^{n-1})(1 - q)^{-1}}, \quad q = \alpha(1 + \beta)$$

The temperature of the inlet gas stream of the catalyst bed mixed with the cold bypass stream may differ from the advisable temperature and moreover may be not uniform. The fluctuations of the inlet gas stream temperature for a catalyst bed can result in:

- temperature non-uniformities emerging in the catalyst bed (the so-called “hot spots”);
- rise in the outlet temperature of the bed, which may result either in increasing the inlet temperatures of the next catalyst beds or in an increased volume of the bypass gas.

In these cases, an unstable reactor operation is possible. To analyse the possible changes in the temperature conditions of a catalyst bed, a study was made on the parametric sensibility to the bed inlet temperature fluctuations using a one-dimensional mathematical model.

The parametric sensibility of a catalyst bed was calculated as follows. First, for chosen bed conditions, the gas composition and the catalyst bed height being known, the temperature profile $T_0(\xi)$ was calculated. Then, the inlet temperature of the bed received an increment of 1° and another temperature profile $T(\xi)$ was calculated for the same gas composition. The divergence of the temperatures $dT(\xi) = T(\xi) - T_0(\xi)$ was calculated for each point of the bed height. The calculation was executed for each catalyst bed.

Fig. 9 shows the calculated temperature sensibility for different catalyst beds of a 4-bed reactor. The initial gas composition was taken in accordance with the purge gas compositions: $\text{CO}/\text{H}_2/\text{CO}_2 = 20.62/64.04/7.56$. The model took account of the changes in the heat capacity of the mixture and in the reagents enthalpy versus the temperature and the reagents composition changing in the course of reaction. The figure demonstrates that the temperature sensibility of a catalyst bed increases along the bed and reaches the value of 1.9–2.3 at the bed outlet. It means that increasing the

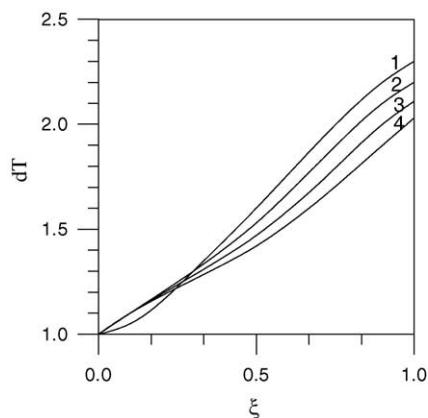


Fig. 9. Dependence of the temperature sensitivity along the dimensionless bed height (ξ) in different catalytic beds: the first bed (curve 1), second (2), third (3) and fourth (4).

inlet temperature of the gas stream by 1° causes the outlet temperature increase by approximately 2° for any catalyst bed. A slight drop in the sensibility of the subsequent beds may be the result of a relative decrease in the reaction rate.

Such estimations of the catalyst beds' parametric sensibility allow an assessment of the permissible temperature non-uniformities for the reaction mixture stream at a bed inlet as well as of divergence in the bypass gas expenditure caused by temperature fluctuations at the catalyst beds' outlets.

The fact that, for a long-term catalyst operation, temperature at a bed outlet should not exceed 410°C implies that the local divergence at a cross-section of the inlet temperature for a catalyst bed should not exceed $8\text{--}10^\circ$. This enables us to formulate the requirements for the mixing device operation.

Note that the fraction of liquid hydrocarbons and water condensed depend on the temperature in separator (Fig. 10). These data were calculated using a program based on the Gibbs energy technique for the reaction components.

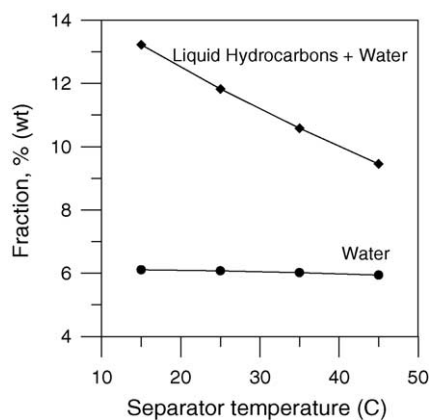


Fig. 10. Dependence of the fractions of liquid hydrocarbons + water and water condensed in separator vs. temperature of separation. $P = 80$ atm.

6. Conclusion

Experimental investigations and mathematical modelling of synthesis gas conversion to hydrocarbon (gasoline range) were carried out. The process was investigated in the temperature range $320\text{--}400^\circ\text{C}$, at pressures $40\text{--}80$ atm, $\text{GHSV} = 500\text{--}20,000\text{ h}^{-1}$, ratio $\text{H}_2/\text{CO} = 2\text{--}10$. The influence of the catalyst composition (catalyst acidity) on the products distribution and the process productivity with regard to the liquid hydrocarbons was studied. It has been shown that the products distribution depends mainly upon the molar ratio H_2/CO and GHSV while the main factors affecting the process productivity and the yield of the liquid hydrocarbons are pressure and temperature in the reactor.

Mathematical modelling of the process flow sheet with the unreacted gas recycled has been performed. The influence of different parameters of the process (the feeding gas composition, the temperature in the reactor, the circulation flow rate, the volume of the purge gas, the contact time of the reaction mixture, the separator temperature, etc.) on the catalyst productivity with regard to liquid hydrocarbons was studied.

The estimation of the catalyst beds' parametric sensibility allows an assessment of the permissible temperature non-uniformities for the reaction mixture stream at a bed inlet. This value should not exceed $8\text{--}10^\circ$.

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