ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В.Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
электрохимии им. Д.В. Сокольского»

NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
JSC «D.V. Sokolsky institute of fuel, catalysis
and electrochemistry»

SERIES
CHEMISTRY AND TECHNOLOGY

4 (436)

JULY-AUGUST 2019

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

Clarivate
Analytics

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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

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«ҚР ҰҒА Хабарлары. Химия және технология сериясы».
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.)
Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 30.04.2010 ж. берілген **№1089-Ж** мерзімдік басылым тіркеуіне қойылу туралы куәлік

Мерзімділігі: жылына 6 рет.
Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

«Известия НАН РК. Серия химии и технологии».
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы)
Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан **№10893-Ж,** выданное 30.04.2010 г.

Периодичность: 6 раз в год
Тираж: 300 экземпляров

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, ком. 219, 220, тел. 272-13-19, 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142,
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News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)
The certificate of registration of a periodic printed publication in the Committee of Information and Archives of the Ministry of Culture and Information of the Republic of Kazakhstan N 10893-Ж, issued 30.04.2010

Periodicity: 6 times a year
Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19, 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Editorial address: Institute of Organic Catalysis and Electrochemistry named after D. V. Sokolsky
142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22,
e-mail: orgcat@nursat.kz

Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2019.2518-1491.40**
Volume 4, Number 436 (2019), 36 – 42

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MODELING PROCESS OF SYNTHETIC LIQUID HYDROCARBONS FUEL PRODUCTION BY COMBINED STEAM-DRY REFORMING OF METHANE OVER Co-CONTAINING MULTICOMPONENT CATALYST

Abstract. The paper is devoted to modeling the stages of a two-step technology proposed by authors for synthetic liquid hydrocarbons (SLH) production from syngas produced by bireforming of methane – combined steam and dry reforming of methane over own developed catalyst. In both processes: bireforming of methane and Fischer – Tropsch synthesis, the samples of the same catalyst containing cobalt, modified by additives of the transition metals of Groups IVth and VIIIth of the Periodic Table and supported on alumina – 5%Co-M1-M2/Al2O3 have been long-term tested (> 100 hours in each process). The obtained experimental results were used as the basis for calculations at modeling the technological circuit for both processes. As software, Aspen HYSYS was used. In the paper, the modeled technological circuits of syngas production by bireforming of methane and production of synthetic liquid hydrocarbons from syngas over the developed catalyst are presented; the material and heat balances obtained at modeling technology are included too.

Keywords: Modeling; Catalyst; Combined Steam-Dry Reforming of Methane; Syngas; Synthetic Liquid Hydrocarbons.

1 INTRODUCTION

Due to the growth of Earth's population and economic development, the demand for energy sources is significantly increasing. That requires searching the new and that is more important the clean energy sources to reduce the negative impact on the environment. Thanks to the larger amount, availability, versatility and less environmental impact, natural gas is becoming the most desirable type of raw material compared to other fossil fuels [1]. Thus, International Energetic Agency (IEA) made forecast that global production of natural gas can be increased by 55% from 2010 to 2035 year [2]. At present time, increasing of global reserves of natural gas/methane occurs, that caused by high rate of exploration and particularly by contribution of shale gas. However, a significant amount of the world's natural gas reserves remain difficult to recover or are located in remote places. Monetization of such reserves is an important task for gas producers and demands for major investments into organization of industry and export/transportation infrastructure [4].

Transportation of energy raw materials in liquid form by oil tankers, rail and road transport is an economical way. However, the large amount of natural gas remaining after compression, even under high pressure, makes it difficult to store and transport over long distances. One of the ways to solve this problem is the GTL technology. GTL is the chemical transformation of gas (methane) into heavier hydrocarbons, which are in a liquid state under atmospheric pressure and can be easily transported [5, 6].

Over the past three decades, GTL technologies have been further developed and allow to the gas producers to expand and diversify their markets through various types of high-quality liquid motor fuels [7], in particular, diesel and jet fuels. The diesel fuel produced by the GTL process has a significantly higher quality than that produced during the processing of crude oil. So, its cetane number is at least 70 compared to 45-55 for most conventional fuels, low sulfur content (less than 5 ppm) and aromatic hydrocarbons (less than 1%) [8]. The global demand for diesel fuel tends to grow and is projected to increase from 25 million to 37 million barrels per day from 2011 to 2035 [9]. Technology of GTL can contribute in meeting this demand.

As a rule, the GTL technologies include three main stages [10]:

1. Production of syngas by catalytic interaction of methane with oxygen containing agent (processes of partial oxidation of methane or steam and bireforming of methane). Ratio of hydrogen to carbon monoxide in syngas produced is varied depending on feed composition;
2. Catalytic Fischer–Tropsch synthesis (FTS) – syngas conversion in FTS reactors of various construction into a wide range of aliphatic hydrocarbons (synthetic oil);
3. Cracking – transformation of the heavy hydrocarbon obtained into high-quality products: naphtha, diesel fuel, lubricants.

Fischer–Tropsch synthesis occurs accordingly to the following reaction (Eq.1):

$$2CO(g) + H_2(g) \rightarrow (–CH_2–)n(l) + CO_2(g) + H_2O \qquad \text{(Eq.1)}$$

FTS is highly exothermic process (140–160 kJ/mol^{-1} of converted CO) and is accompanied by the formation of some amount of carbon dioxide and water along with the production of liquid hydrocarbons [11]). The main FTS reactions compete with methanation (Equation 2) and reactions leading to the formation of propane and butane (LPG), which are very exothermic:

$$CO + 3H_2 \rightarrow H_4 + H_2O \qquad \text{(Eq.2)}$$

In order to ensure the preferential running of the FT reaction, the synthesis is carried out at low temperatures: 220–350°C; pressure: 2–3 MPa over the carefully selected catalysts (usually cobalt or iron) in reactors that promotes the growth of long-chain hydrocarbons. Nowadays, only Sasol and Shell have constructed the large-scale industrial plants – Oryx and Pearl, respectively.

There are two main categories of FTS technologies – high and low temperature synthesis, which differ in type of applied catalyst – Fe and Co respectively, composition and distribution of the products [12-14]. Commonly the yield of diesel fuel at FTS plants is about 70% that is much higher than for processing crude oil – about 40% [15]. A great advantage of FTS technologies is their focus exclusively on producing the high-value light and medium distillates, in contrast to traditional oil refining, where a significant amount of low-value fuel oil is formed. The proportion of middle distillates in the products composition is about a third higher than for conventional refining [16].

The main ways of syngas producing are partial oxidation, auto thermal reforming, and combined steam-dry reforming of methane [17-20]. Disadvantage of first two processes is high dilution by nitrogen both of the inlet gas stream and the final reforming products, when air is used as an oxidant; in case of pure oxygen use, the need of its extraction from the air and storage is appeared. It is economically unprofitable and technically unsafe. As for the processes of dry and steam reforming, the H_2/CO ratio in the resulting synthesis gas is lower (<2) or higher (> 3) respectively than the optimum ratio for FTS.

One of the ways for production of syngas with required composition is combination of steam and dry reforming, the so-called bireforming of methane. Its main disadvantage is strong endothermicity and, as a result, high energy intensity of process as a whole. That can be compensated by integration of energy streams of natural gas reforming reactor (endothermic process) and of Fischer–Tropsch reactor (exothermic process). In general, bireforming process has the following essential advantages:

1) H_2/CO ratio of obtained syngas can be optimized for the specific catalyst;

2) carbon dioxide and water formed in Fischer–Tropsch process can be recycled to the process of syngas production;

3) opportunity to utilize the alternative sources of carbon, like biogas.

Currently, to solve the issue of the appropriateness of the use of various technological processes and schemes, the various software products developed by companies or researchers for their own and/or commercial needs are widely used [21]. The Aspen HYSYS and Aspen Plus packages are the most common used software. These software products are used to scale the processes studied in the laboratory as well as to determine the feasibility of their commercialization, and to find ways to optimize existing technological processes.

The present work deals with simulation of technology for two stages of GTL process: production of syngas by bireforming of methane and production of synthetic liquid hydrocarbons by Fischer–Tropsch synthesis over the developed Co-containing catalyst using software package Aspen HYSYS.

2 EXPERIMENTAL

To simulate both the syngas production by bireforming of methane and the production of synthetic liquid hydrocarbons by conversion of syngas formed at the first step over the developed Co-containing catalyst, the software package ASPEN HYSYS was used. It includes five modes for modeling of chemical reactions proceeding (so called types of reaction), which are differed by type of incoming data:

- ***conversion reaction*** – for this type of reaction, the stoichiometry of reaction and conversion degree of base component on reactor's outlet are specified;
- ***equilibrium reaction*** – equilibrium constant is specified as temperature function either as formula or as table;
- ***kinetic reaction***, including three options – the parameters are kinetic data (the reaction orders by reactants, the constants of direct and reverse reactions, the appropriate activation energies and pre-exponential factors).

Due to absence of data on kinetic parameters of processes studied to simulate both bireforming and Fischer–Tropsch synthesis the first type of reaction was chosen – *Conversion reaction*. In process of modeling, a number of assumptions were made: all reagents are chemically pure and carbon deposition is absent. The last assumption based on the fact that catalyst studied in dry reforming of methane (more active process towards carbon deposition compared to other type of methane conversion) did not demonstrate decrease in its activity during continuous long-term testing for more than 100 hours.

For modeling, the data obtained during testing the 5%Co-M1-M2/Al_2O_3 catalyst prepared by impregnation method in both processes – the bireforming of methane and Fischer–Tropsch synthesis were used. Bireforming was carried out under the following conditions: CH_4/CO_2 ratio on inlet of reactor was 1:1, steam amount – 25 vol.%, GHSV=1250 h^{-1}, pressure – 1 atm, t = 700°C. The degrees of methane and carbon dioxide conversion are 94.8% and 61.7% respectively. FTS process was carried out under pressure of 1.0 MPa, temperature – 233°C, ratio of H_2:CO=2:1, GHSV=4000 h^{-1} over the fresh sample of the same catalyst.

3 RESULTS AND DISCUSSION

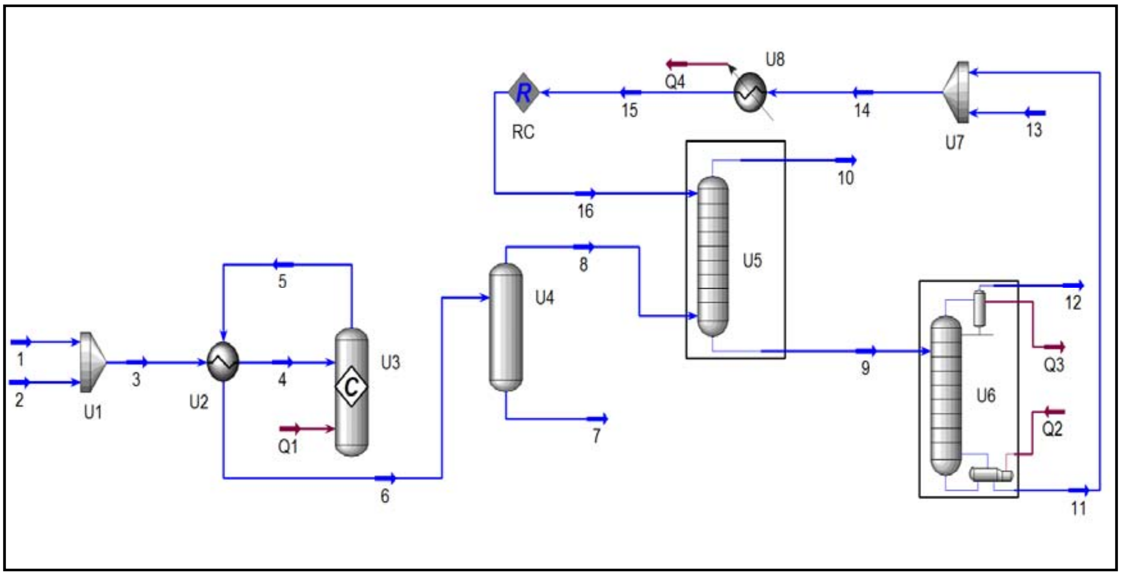
3.1 Technological scheme for combined steam-dry reforming of methane

The technology of production and processing of synthesis gas has been modeled using Aspen HYSYS software and based on the general principles for calculations of the mass and energy balances of technological schemes. The software includes a set of auxiliary subsystems to provide the solutions for chemical-technological processes.

To make a model for combined steam-dry reforming of methane (bireforming of methane), the technological parameters corresponding to the experimental data obtained during the long-term testing of the 5% Co-M1-M2/Al_2O_3 catalyst for 100 hours were used. Also, the reactor-converter was used to simulate the technology.

In Figure 1, the technological scheme of synthesis gas production by bireforming of methane is presented. A model includes the following streams of products and energy described below.

Carbon dioxide and methane (1) enter the mixer U1 to be mixed with steam, part of which is returnable due to contribution of both unreacted water after the bireforming of methane as well as water formed after Fischer-Tropsch synthesis. Then, the mixture of gases (3) passes through the heat exchanger U2, where heat exchange takes place between the streams of the initial products (inlet) and the products after the reactor (outlet flow with temperature is about 700 ° C). After the heat exchanger U2, the heated mixture (4) enters an isothermal reactor U3 filled with the fixed bed catalyst – 5%Co-M1-M2/Al_2O_3 heated by external energy flow Q1 to maintain the process temperature is about 700°C. Then, the hot gases (5) including reaction products – hydrogen and carbon monoxide as well as unreacted water, methane, and carbon dioxide are directed to the heat exchanger U2, where they are cooled and then stream (6) is sent to separator U4 for separation of unreacted water (7). The mix of gases (8) – hydrogen, methane, and carbon oxides are passed through the absorber U5 irrigated with a solution of monoethanolamine to absorb unreacted carbon dioxide and release synthesis gas with residues of unreacted methane (10), which is sent to the FTS reactor. The carbon dioxide enriched monoethanolamine solution (9) is sent to the regenerator U6, where it is separated into carbon dioxide (12) and the monoethanolamine solution, then the latter is diluted with makeup water (13) to the desired concentration in the mixer U7, is cooled in the refrigerator U8, and is sent to the recycling RC to be reused in the absorber U5.



1 – methane and carbon dioxide; 2 – steam; 3 – steam-gas mixture; 4 – heated gas mixture; 5 – reaction products + unreacted raw materials; 6 – cooled products; 7 – condensate, 8 – raw synthesis gas, 9 – monoethanolamine saturated with carbon dioxide; 10 – synthesis gas purified from CO_2; 11– regenerated monoethanolamine; 12 – carbon dioxide; 13 – feed water; 14 – monoethanolamine for recycling; 15 – cooled monoethanolamine; U1 – mixer, U2 – heat exchanger, U3 – conversion reactor; U4 – separator; U5 – absorber; U6 – monoethanolamine regenerator; U7 – mixer; U8 – refrigerator; Q1, Q2, Q3, Q4 – energy flows; RC – recycling

Figure 1 – Technological scheme for synthesis gas production by bireforming of methane

A summary mass balance for the synthesis gas production technology is given in Table 1.

Table 1 – Summary mass balance of technology for the synthesis gas production by bireforming of methane over the 5%Co-M1-M2/Al_2O_3 catalyst

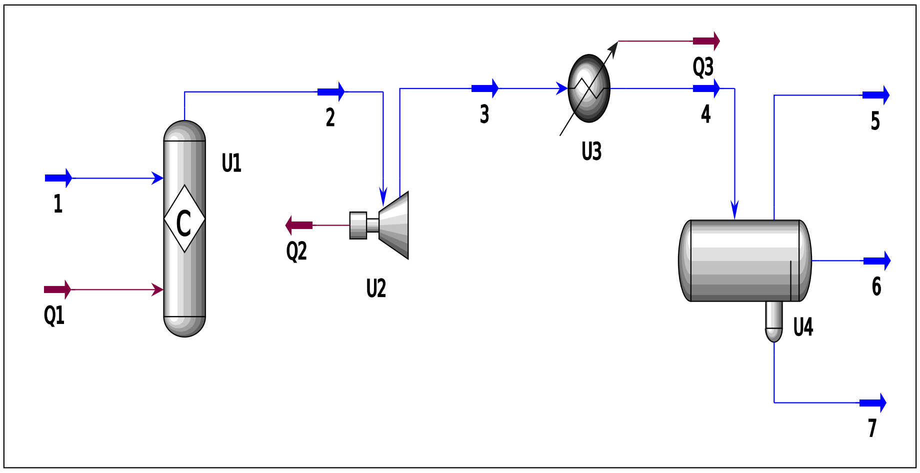
Input, Mass IN	Kg/h	Output, Mass OUT	kg/h
CO_2	110.0243	CO_2	0.4777
H_2O	18.0151	H_2O	0.1083
CH_4	40.1073	CH_4	2.0710
H_2O(feed)	1.8015	H_2	11.2978
		CO	107.9750
		Losses	48.0180
TOTAL	169.9482	TOTAL	169.9478
	100%		100%

3.2 Technological scheme for synthetic liquid hydrocarbon production by FTS

The synthesis gas (1) produced at the previous stage by the combined steam-dry conversion of methane enters the isothermal reactor U1 for Fischer-Tropsch synthesis. The mix of reaction products and unreacted reagents (2) pass through the expander U2, where the pressure is reduced to atmospheric one. After expander, the partially cooled mix of products (3) enters the refrigerator U3, then the cooled products (4) are sent to a three-phase separator U4, where the products are divided into three phases: gas (5), organic (6) and water (7) (Fig.2).

The main products of the Fischer-Tropsch synthesis are the C_{5+} fraction – synthetic liquid hydrocarbons (SLH) mainly composed of n-alkanes. The selectivity of their formation is about 80%. Also, methane, water, C_2-C_4 hydrocarbons, and carbon dioxide formed during FTS and unreacted hydrogen and carbon monoxide are presented in product flow after reactor.

The mass balance of the FTS reactor, where the process occurs over the 5%Co-M1-M2/Al_2O_3catalyst is presented in Table 2.



1 – synthesis gas produced at the previous stage; 2 – reaction products and unreacted substances; 3 – products under atmospheric pressure; 4 – cooled products; 5 – mix of hydrocarbons, unreacted synthesis gas, and CO_2; 6 – C_{5+} hydrocarbons, 7 – water; U1 – FTS reactor; U2 – expander; U3 – refrigerator, U4 – three-phase separator; Q1, Q2, Q3 – energy flows

Figure 2 – Technological scheme for Fischer-Tropsch synthesis

Table 2 – Mass balance of reactor for FTS over 5%Co-M1-M2/Al_2O_3 catalyst

Input	Amount, Kg/h	Output	Amount, Kg/h
Hydrogen	13.4400	Hydrogen	1.7898
Carbon monoxide	93.3697	Carbon monoxide	18.6737
		Carbon dioxide	0.9699
		Methane	2.6855
		Water	47.2464
		$\sum C_2$-C_4	2.7634
		$\sum C_{5+}$	32.6786
TOTAL	106.8097	TOTAL	106.8073

In Table 3, the energy balance of the Fischer-Tropsch synthesis reactor is given.

Table 3 – Energy balance of reactor for FTS over 5%Co-M1-M2/Al_2O_3

Input	MJ/h	%	Output	MJ/h	%
H_2+CO	312.2398	33.82	Gases	118.9012	12.88
Q_1	442.5103	47.92	SLH	60.7977	6.58
Q_2	31.3409	3.39	Water	743.6607	80.54
Q_3	137.2686	14.87			
TOTAL	923.3597	100	TOTAL	923.3597	100

Thus, the simulation of the two main stages of the GTL process – the production of synthesis gas and its processing including calculations of mass and energy balances confirms the high efficiency of the proposed technology for the production of synthetic liquid hydrocarbons over the developed – 5%Co-M1-M2/Al_2O_3.

CONCLUSION

Earlier by means of Aspen HYSYS software, the authors have simulated the process of methane bireforming over the 5%Co-M(9:1)/Al_2O_3-5%REE-1 catalyst performed the high degrees of methane and carbon dioxide conversion [22]. In present work, bireforming was modeled using another Co-containing catalyst showed lower conversion both of methane and carbon dioxide – 94.8% and 61.7% respectively at 700°C. In addition, Fischer–Tropsch synthesis over the same catalyst was modeled.

As a fist approximation, the simulated technology for the two-stage production of synthetic liquid hydrocarbons from syngas obtained by bireforming of methane using developed catalyst – 5%Co-M1-M2/Al_2O_3 demonstrates its viability. Such technology is applicable in remote areas of gas production. Liquid hydrocarbons formed consist mainly of n-alkanes. The fraction corresponding to diesel fuel is a final commercial product. The resulting liquid products can be easily transported to places where they can be further refined.

In the future, it is planned to combine the two stages – production of syngas and its conversion by FTS into one integrated technological scheme including the step of compression of the syngas obtained at first stage up to pressures required to perform FTS over the developed catalyst/catalysts.

Acknowledgement: This research was supported by the Ministry of Education and Science of the Republic of Kazakhstan, the Program # BR05236739 MES RK.

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Co ҚҰРАМДЫ КӨПКОМПОНЕНТТІ КАТАЛИЗАТОРДА МЕТАННЫҢ БУЛЫ КӨМІРҚЫШҚЫЛДЫ РИФОРМИНГІМЕН ЖҮРЕТІН ССК ӨНДІРІС ТЕХНОЛОНИЯСЫН МОДЕЛДЕУ

Аннотация. Бұл жұмыс авторлармен ұсынылған жеке катализаторлардың қолданылуымен метанның біріктірілген – булы көмірқышқылды және булы риформингі жолымен алынатын синтез-газдан синтетикалық сұйық көмірсутектерді (ССК) өндіру технологиясының екі сатысының әрқайсын моделдеуге арналған. Екі процесте де (метанның көмірқышқылды конверсиясы және Фишер-Тропш синтезі) алюминий тотығына қондырылған және периодтық жүйенің 4 және 8-ші топ ауыспалы металдар қоспасымен модифицирленген кобальт негізіндегі жалғыз катализатор 5%Co-M1-M2/Al_2O_3 ұзақ және үздіксіз (әрбірі 100 сағаттан артық) тестілеуден өтті. Алынған тәжірибелік нәтижелер әрбір процестерге арналған технологиялық сұлбаны моделдеу кезінде есептеулердің негізіне еңгізді. Бағдарламалық қамтамасыз ету ретінде Aspen HYSYS өнімі қолданылған болатын. Жұмыста жасалған катализаторда метанның булы көмірқышқылды риформингі жолымен синтез-газды өндірудің және синтез-газдан синтетикалық сұйық көмірсутектерді алудың технологиялық сұлбасы келтірілген, моделдеу барысында алынған материалдық және жылулық баланс есептелген.

Түйін сөздер: Моделдеу; Катализатор; Метанның Булы көмірқышқылды Конверсиясы; Синтез-газ; Синтетикалық Сұйық Көмірсутектер.

УДК .001.57; 665.644.4; 547.211; 546.264-31

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МОДЕЛИРОВАНИЕ ТЕХНОЛОГИИ ПРОИЗВОДСТВА СЖУ ПУТЕМ ПАРОУГЛЕКИСЛОТНОГО РИФОРМИНГА МЕТАНА НА Co-СОДЕРЖАЩЕМ МНОГОКОМПОНЕНТНОМ КАТАЛИЗАТОРЕ

Аннотация. Работа посвящена моделированию стадий предлагаемой авторами двухстадийной технологии производства синтетических жидких углеводородов (СЖУ) из синтез-газа, получаемого путем пароуглекислотного риформинга метана – комбинированный углекислотный и паровой риформинг метана, с применением собственных катализаторов. В обоих процессах: пароуглекислотная конверсия метана и синтез Фишера-Тропша, длительно и непрерывно (более 100 часов в каждом процессе) тестировались образцы одного и того же катализатора на основе кобальта, модифицированного добавками переходных металлов 4-ой и 8-ой групп Периодической системы, нанесенного на оксид алюминия – 5%Co-M1-M2/Al_2O_3. Полученные экспериментальные данные легли в основу расчетов при моделировании технологической схемы каждого процесса. В качестве программного обеспечения был использован продукт Aspen HYSYS. В работе приведены технологические схемы производства синтез-газа путем пароуглекислотного риформинга метана и получения синтетических жидких углеводородов из синтез-газа на разработанном катализаторе, рассчитаны материальные и тепловые балансы, полученные в ходе моделирования.

Ключевые слова: Моделирование; Катализатор; Пароуглекислотная Конверсия Метана; Синтез-Газ; Синтетические Жидкие Углеводороды.

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ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Редакторы: *М. С. Ахметова, Т. А. Апендиев, Аленов Д.С.*
Верстка на компьютере *А.М. Кульгинбаевой*

Подписано в печать 05.08.2019.
Формат 60х881/8. Бумага офсетная. Печать – ризограф.
5,25 п.л. Тираж 300. Заказ 4.

Национальная академия наук РК
050010, Алматы, ул. Шевченко, 28, т. 272-13-18, 272-13-19