К недостаткам гидродинамических передач необходимо отнести:

- переменный КПД в различных режимах работы и его меньшее значение по сравнению с КПД механической передачи;
- высокая стоимость и сложность изготовления по сравнению с механическими передачами;
- необходимость охлаждения рабочей жидкости;
- трудности в создании надежных и долговечных уплотнений.

Таким образом, подводя итоги можно сделать следующие выводы. Разработанные на сегодняшний день схемы и конструкции приводов, свидетельствуют о том, что они могут выполнять не только функции передачи мощности от двигателя к рабочим элементам и преобразование вращательного движения в поступательное, но также обеспечивать защиту от поломки при перегрузках, дискретное или адаптивное управление режимами работы оборудования, изменять режимы в функции технологической нагрузки и др.

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Synthesis of alcohols by direct syngas conversion, produced by reprocessing of vegetable-and-oil raw materials

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Abstract

The influence of C-containing bimetallic catalysts on the synthesis of alcohols from syngas, produced by gasification of mixed vegetable wastes and heavy oil residues is investigated. The efficiency of C-containing iron catalysts modified with cobalt in the process of synthesis of monoatomic fatty alcohols by direct conversion of syngas has been experimentally determined.

Keywords: syngas, catalytic conversion, alcohols, gasification, biomass, heavy oil residues.

Introduction

Alcohols, in particular higher fatty alcohols, are one of the most important products of petrochemical synthesis that are widely used in industry for producing plasticizers, solvents,

surfactant, fragrant substances lubricating oils, hydraulic fluids, and as a high-octane additive to motor gasoline.

More than 2 million tons of higher fatty alcohols (HFA) are produced in the world annually. Since 1960th, after discovery and introduction of hydroformylation reaction the main industrial way of synthetic HFA production has become oxosynthesis process instead of outdated "isobutyl oil synthesis" technology [1], that is carried out in two coherent catalytic stages: hydroformylation of olefins (1) and hydrogenation of intermediate aldehydes into alcohols (2):

However, it should be noted that this technology is very sensitive to process conditions (syngas composition, temperature, pressure), as well as to the composition of olefin feedstocks and the structure of the ligand, that's part of the catalytic complex. Thus, hydroformylation of olefin mixtures is carried out in several stages due to the fact, that because of different reactivity of olefin isomers it is difficult to achieve high degree of conversion and simultaneously high selectivity in the process of their joint hydroformylation into one stage.

Despite the existing developments to improve the efficiency of the hydroformylation process [e.g., 2-4], this technology remains very complex and expensive.

The possibility of direct conversion of syngas into higher fatty alcohols using cheaper catalytic systems is of great scientific and practical interest:

Along with traditional methods of producing syngas from hydrocarbon raw materials, the development of the technology for syngas production with the involvement of renewable raw materials - biomass - seems promising [5].

Two types of catalysts are used to study the synthesis of monatomic alcohols from CO and H₂: modified zinc-chrome catalysts for methanol synthesis and modified Fischer-Tropsch synthesis catalysts [6]. At present, the latter are preferred because they work in softer conditions and exhibit greater selectivity with respect to the formation of C₂₊ monatomic alcohols. Typically, iron catalysts are modified because they are more prone to oxidizing. The key task of research in this field in order to go beyond the scope of experimental is the development of catalysts with high activity per pass and highly selective with respect to HFA. In this regard, catalysts containing carbon materials as carriers are of some interest [7, 8].

Materials and methods

Preliminary experiments have shown that carbon has a positive effect on the selectivity of iron catalysts in the synthesis of single atomic alcohols from CO and H₂. The introduction of cobalt into the catalyst usually allows to increase the length of formed hydrocarbon chains. Based on this fact, we used C-containing iron catalysts modified with cobalt for studies of syngas conversion into monatomic fatty alcohols. Metal-carbon composite material was prepared by calcinating of starch/microcrystalline cellulose (MCC) with cobalt and iron salts in an inert medium at 500 °C.

Syngas conversion with the use of experimental samples of prepared catalysts was carried out on a gas-flow laboratory catalytic unit with a stationary catalyst bed (Fig. 1).

Fig. 1. Scheme of laboratory catalytic unit with a stationary catalyst bed

1 - compressed gas cylinders; 2 - gas holder; 3 - compressor; 4 - buffer tank; 5, 10 - pressure regulators; 6 - system of catalytic purification of syngas from oxygen; 7 - electronic gas flow meter; 8 - reactor; 9 - separators; 11 - gasometer; 12 - gas flow control; M - pressure gauges

The synthesis of alcohols from CO and H₂ was carried out at 260-300 °C, pressure 20-30 atm, volume velocity 1000-1200 h⁻¹, duration of the process 5-6 h.

Liquid synthesis products were analyzed by gas-liquid chromatography.

For experiments, gas mixtures were prepared that simulate the composition of gasification products of three-component mixtures "vegetable wastes - fuel oil - water" (Table 1).

Table 1

Generating gas composition

Raw material mixture composition	Gas composition, vol. %					H ₂ :CO
	H ₂	CO	CO ₂	N ₂	CH ₄	
Fuel oil (15%)+water (5%) + sunflower seed shells (80%)	20,7	9,8	7,9	60,5	1,1	2,1
Fuel oil (15%)+water (5%) + corn corbs (80%)	18,9	8,9	7,9	63,4	0,9	2,1
Fuel oil (20%) +water (10%) + corn corbs (70%)	17,9	9,3	10,6	61,2	1,0	1,9

It has been established that addition of water to vegetable-and-oil raw materials and its preliminary mechanical activation have a positive impact on the chemical process of gasification: the formation of carbon dioxide is reduced and the yield of target components - CO and H₂ is increased. The ratio of H₂:CO in generator gases is close to or greater than 2, that makes such syngas quite suitable for conversion into alcohols and other organic products after its proper purification and preparation [9]. At the same time, we have previously established that hydrocarbons and monatomic alcohols can be obtained by using the generating gases produced by biomass gasification without conditioning, i.e. without bringing their composition to the stoichiometric ratio of syngas [10].

Results

In the course of syngas conversion experiments using experimental samples of prepared catalysts, the impact of the initial carbon matrix on the synthesis process was initially investigated. The results are presented in Table 2.

Comparative analysis has shown that the use of MCC-based catalyst provides a slightly higher degree of CO conversion and a lower total yield of liquid products (liquid hydrocarbons + alcohols), however, the alcohol/hydrocarbons ratio exceeds 1. The starch-based catalyst is characterized by a higher throughput of liquid products and a lower degree of gas formation.

Table 2

The impact of the original carbon matrix on the synthesis process

Matrix type	Process data				
	CO Conversion, %	Liquid hydrocarbons yield, g/m ³	Alcohols yield, g/m ³	Gas yield, %	Catalyst capacity for liquid products, g/kg Kt·h
Starch	91	107	86	15	841
MCC	95	76	92	35	754

Further studies were carried out with catalysts with different amounts of modifying additives, as it was found that the cobalt content in C-containing iron catalysts has a significant impact on the synthesis of monoatomic alcohols produced from syngas. Bimetallic (20% Co+Fe) catalysts containing 7% Co (Co: Fe = 1 : 2), 10% Co (Co: Fe = 1 : 1), 13% Co (Co: Fe = 2 : 1) and a monometallic iron catalyst were used for experiments.

Fig. 2 shows the influence of cobalt content in catalysts on their capacity for liquid synthesis products and, in particular, for alcohols.

Figure 2 – Influence of cobalt content on catalyst capacity:
1 - for liquid products; 2 - for alcohols

It's clear that the increase in cobalt content leads to a significant increase in the activity of the catalyst and has a positive effect on its productivity. Maximum achieved capacity for liquid products is 841 g/kg Kt·h, for alcohols - 370 g/kg Kt·h. However, these figures are decreasing if a cobalt content in catalyst more than 10%. At the same time, catalytic systems with a capacity of at least 150-200 g/kg Kt·h are considered to be economically promising for the synthesis of alcohols from CO and H₂ [11].

Curves on the figure 3 reflect the influence of cobalt content in catalysts on other synthesis process indicators.

It is shown, that with the increase of cobalt content in the catalyst the increase of CO conversion rate from 77 to 99% is observed. The gas yield firstly decreases from 61 to 15%, but at the ratio of Co : Fe = 2 : 1 it increases sharply to 57%. The yield of liquid products also increases with increasing cobalt content, reaching maximum - 107 g/m³ for liquid hydrocarbons and 86 g/m³ for alcohols with a ratio of Co : Fe = 1 : 1. The increase of this ratio towards cobalt leads to deterioration of this indicator.

Figure 3 – Influence of cobalt content on the synthesis process: 1 - CO conversion, %; 2 - gas yield, %; 3 - liquid hydrocarbon yield, g/m³; 4 - alcohol yield, g/m³

Conclusions

So, there was experimentally established that the developed C-containing bimetallic catalysts can be used for direct conversion of syngas into monoatomic alcohols. The obtained chemical analysis data of synthesis products allow to make conclusion about high selectivity of catalysts (more than 85%) to higher fatty alcohols (C₆-C₉) formation. Catalyst with an optimal ratio of components Co : Fe = 1 : 1 provides maximum productivity on products and is promising for commercial use in the technology of co-processing vegetable wastes and oil residues into valuable chemical products.

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