Catalytic cracking of vacuum gas oil by using the aerosol nanocatalysis on new modification catalyst WO_3/Si-Zr

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Abstract:

Ukrainian scientists have formulated a new direction in the technology of gas-phase chemical processes – it was called the aerosol nanocatalysis(AnC).The purpose of this research is development of the theoretical foundations of technology aerosol nanocatalysis in the cracking of vacuum gas oil with the use of technology in aerosol nanocatalysis vibration layer of the catalyst system to obtain gasoline and diesel fraction The temperature in the new process is at 250Cº lower than in industrial cracking process , and the amount of catalyst is reduced to a concentration of 2.38 g/m^3 reactor . the WO3/Si-Zr – catalyst at conditions of the new technology displayed higher than 99 % of selectivity of light products formation.

Keywords: catalytic cracking, aerosol nanocatalysis , gasoline , diesel .

Introduction:

Process of catalytic cracking is the largest process, that allows to increase the depth of oil refining, to obtain valuable products, i.e. gasoline and diesel fractions.

The overall productive capacity of catalytic cracking units in USA is higher than 250 million tons/year of the raw materials. This process has gained a very wide development in the countries of Western Europe. The total capacity of catalytic cracking units has reached 35% in U.S. (13.9% in Western Europe, and 6.0 % in Russia) of the capacity of primary oil refining [5, 12, and 18].

In the 60s of the past century, it was discovered the high activity of zeolites in cracking reaction. in this regard , in cracking process they started to use catalysts with Y-zeolite content ($Me_{2/n}O.AL_2O_3.XSiO_2.yH_2O$) not more than 20% wt , which resulted in a significant growth of the yield of desired products of the process , especially at the transition to the cracking of heavy feeddstocks.In order to utilize from all advantages of zeolite catalyst , they began

To use new types of reactor– regenerator devices : at first was the fluidized bed reactor , and then the lift – reactor .thus, the process of catalytic cracking became the fastest growing in the oil refining .Gasoil and diesel fuel in the rural economy needs [4,17] .

In the Technological Institute of East Ukraine Volodymyr Dahi National University - Ukraine (Severodonetsk)at the Department of Technology of Organic Substances ,fuel and polymers . Perspective studies on the cracking of vacuum gas oil aerosol nanocatalysis (AnC) was carried out. The essence of nanocatalysis aerosol technology is to apply a continuous mechano-chemical activation of the catalyst directly in the reaction volume, resulting in required amount of catalyst is reduced to 1-2 g/m^3 reactor, and the activity increases in 105-106 times.

Already conducted studies of the properties of various catalysts (Nexus-345p, zeolite Y, Zr-Si catalyst) under AnC conditions, showing the possibility of increasing the yield of light products in 1.14 times, reduce the volume to 10 times the reactor and the volume of the regenerator to 1500 times compared to existing technologies.This work is a logical continuation of research in this direction,and its main purpose is to study the kinetic characteristics of the new modification Wo_3/Zr-Si catalyst under conditions AnC with the subsequent creation of the foundations of catalytic cracking technology with enhanced technical - economic indices.

Experemental work:

Cracking of vacuum gas oil at conditions of aerosol nanocatalysis conducted on laboratory installation shown in Figure (1).

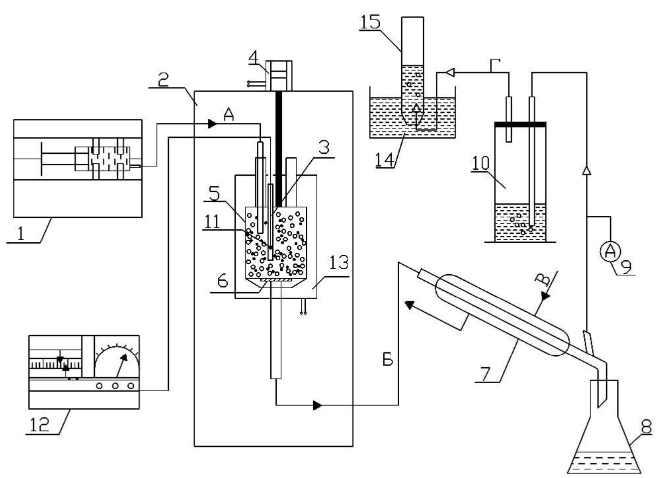

Fig. (1) Laboratory installation for research cracking of vacuum gas oil by aerosol technology nanocatalysis

1 - The dispenser gas oil; 2 - heat chamber; 3-pocket for thermocouple 4- vibrating device5 - reactor;

6- metal-clothed filter 7- condenser 8 - receiver of liquid reaction products; 9 - Analytical selection of gas fraction; 10 – gas washer; 11 - thermocouple; 12 - regulator for frequency and temperature;

13 - Heater; 14 – vessel with water; 15 - collector the gas phase.

Vacuum gas oil, fed in the reactor (5) by the dispenser (1) The reactor is located in heat chamber (2) and was heated by heater (13). The cracking reactions took place in the reactor. The temperature in the reaction zone is measured by a thermocouple (11), and is supported by regulator (12). To prevent outlet of catalyst from the reaction zone is achieved by using a metal cloth filter (6).After, the reactor products go through condenser (7),cooled by water, and entered into the receiver of liquid fraction products (8), the line of gas cracking contain point sampling for analysis (9) and enter into gas washer (10),where its bubbled through the water layer, and then passed through water vessel (14)and entered into a receiver of gas phase (15).The reactor is subjected to reflexive and translational motions with the assistance of vibrating device (4), frequency of oscillation was provided and controlled by regulator (12).

The catalytic system AnC consists of a powder catalytically active material with initial particles diameters of 200 microns and dispersing solid material (dispersing material) with a diameter of 1.0-1.2 mm.Both kinds of particles in a reactor are in constant motion. These conditions allow the synthesis of nanoparticles of different sizes by mechanical effect on the initial particle catalyst of the dispersing materials.

In previous works were found, that before the beginning of the experiment, there must be a preparation of materials to the catalytic system. Specific feature of AnC is adhesion (view of sorption) of the catalyst, dispersing on the surface of the material. And this is necessary to ensure maximum adsorption of catalyst particle under conditions of vibration of the reactor. This allows the determination of the amount of catalyst in the gas phase.After the end of the cracking process liquid phase is taken to the Distillation apparatus ULAB-1-42A, for the analytical determination of the content gaseous reaction products using gas chromatographs:

ЛХМ-8, ЦВЕТ-500(ethylene and hydrogen determined with accuracy not less than 0.01% vol.) [19].Composition and octane number (research method) gasoline fraction determined on a chromatograph CRYSTAL-5000 .

Discussion of results and diagrams:

Experiments were conducted at temperatures 300 ^{0}C, 350 ^{0}C, 400 ^{0}C, 450 ^{0}C, 500 ^{0}C, 550 ^{0}C, and at frequency of mechanochemical activation (MCA) 4, 4.5, 5, 5.5, 6, 6.5, 7 Hz.

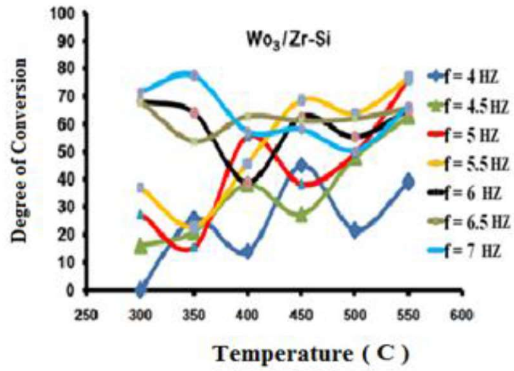

Fig. (2) Comparison of variation curves for conversion degree (% wt) vs. temperature (^{0}C) for WO_3/Si-Zr – catalyst

The maximum degree of conversion (more than 80%) for the examined interval of parameters was observed at 350 ^{0}C and at a frequency mechanochemical activation (MCA) of 7 Hz as shown on (Fig.2) that was obtained at similar condition at the frequency of MCA 6.5 Hz, the temperature is of low effect to the reaction rate. All orders of investigated frequencies MCA in the catalyst complied a tendency to increase degree of conversion with increasing temperatures. Moreover, there are some highs on rising curves at 450 C^o, possibly, the presence of a maximum connected with the fact that at low temperatures, is observed an intensive MCA surface of a catalyst, which then becomes less intensive due to the temperature Softening of the catalyst or catalytic activity combined with a thermal decomposition of hydrocarbons.

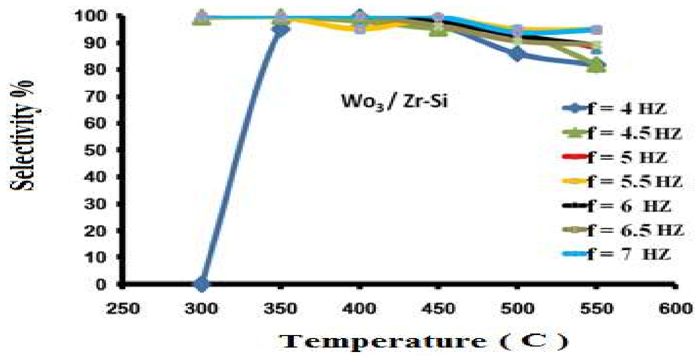

Fig. (3) Comparison of variation curves for the selectivity of the reactions of cracking (%) vs. temperature (^{0}C) for the Catalyst WO_3/Si-Zr

Research of the Catalyst WO3 / Si-Zr showed ,that the selectivity of light fractions above 95% is retained in the interval temperature 300- 450 0C for the whole research at the range frequency MCA. At a frequency MCA of 4 Hz a selectivity above 95% appears at 350 Cº. A further increase of temperature to 550Cº, selectivity of formation light products is reduced to 80-85%.

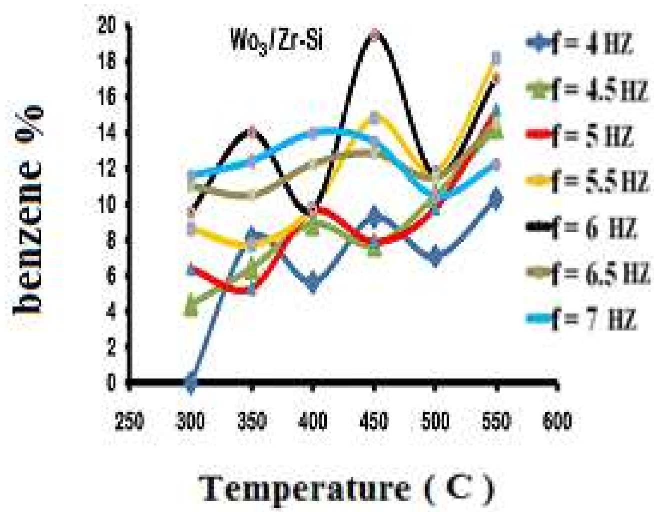

Fig. (4) Comparison of variation curves for the gasoline fraction (%) vs. temperature (^{0}C) for the Catalyst WO_3/Si-Zr

The yields are virtually identical and complex manner dependent on temperature. The maximum achieved output for gasoline fraction was 20% at 450^{0}C and 6 Hz.

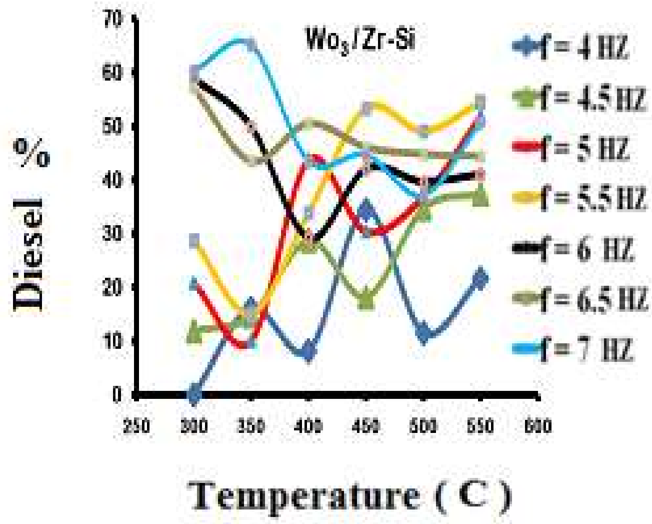

Fig. (5) Comparison of variation curves for the diesel fraction (%) vs. temperature (0C) for catalyst WO_3/Si-Zr

Cracking of vacuum gas oil by aerosol nanocatalysis proceeds with predominant formation of the diesel fraction (180-3500C). The maximum achieved output to the diesel fraction for the catalyst WO3/Si-Zr is 70%.Curves output changes of diesel fraction have a complex dependence with the presence of the maximum at different temperatures for different frequencies MCA.This is possible to explain the influence on activity catalyst, the various technological parameters: temperature, frequency MCA, etc.Their various combination gives the optimal conditions for creating of maximum activity of the catalytic system, at which and are observed high yields of diesel fraction.

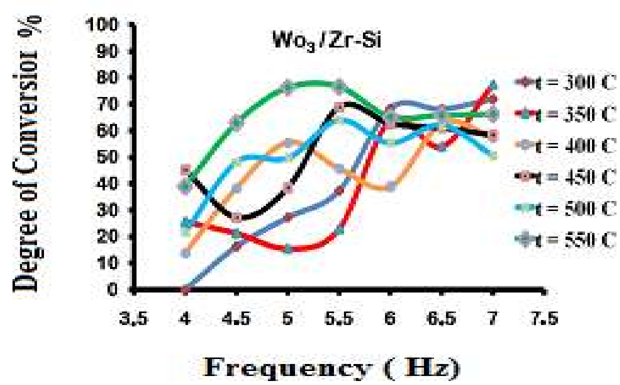

Fig.(6) Comparison of variation curves for the conversion degree (% wt) vs. frequency of vibration (Hz)for catalyst WO_3/Si-Zr

Comparison of the effect vibration frequencies has shown availability general trends to increase the degree of conversion at increasing the frequency MCA in the entire interval investigated parameters.

Thus, traditionally peaks are observed in the curves. Also noted is the stable activation of the surface catalyst from 6 Hz, which in turn led to the degree of conversion of 70%.

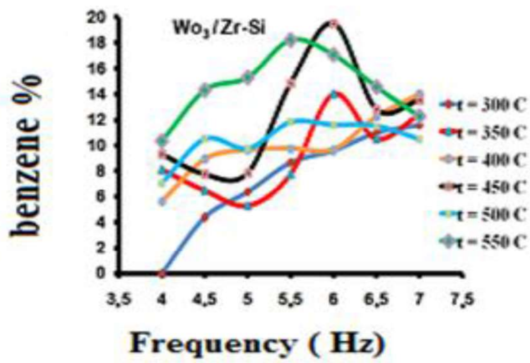

Fig.(7) Comparison of variation curves for the gasoline fraction (%) vs. frequency of vibration (Hz)for catalyst WO_3/Si-Zr

Output of gasoline fractions is considerably lower than the output diesel fraction. Increased frequency MCA leads to higher content of the gasoline fraction in the cracking products the interval temperature and frequency MCA.For temperatures of 350, 450, 550^0C curves of output of the gasoline fraction pass through a maximum. For 350, 450^0C optimum frequency MCA was 6Hz,for 550^0C optimum frequency reduced till 5.5Hz. It can be assumed, that correlation exists between the influenced frequency MCA and temperature. A lower temperature of the process is required to achieve the maximum output of gasoline at these conditions. By a change of MCA frequency, there can be an increase in the output of gasoline fraction depending on the selected process temperature. At high (450-550^0C) temperatures showed a maximum yield of the diesel fraction at the optimum frequency MCA 5.5 Hz.

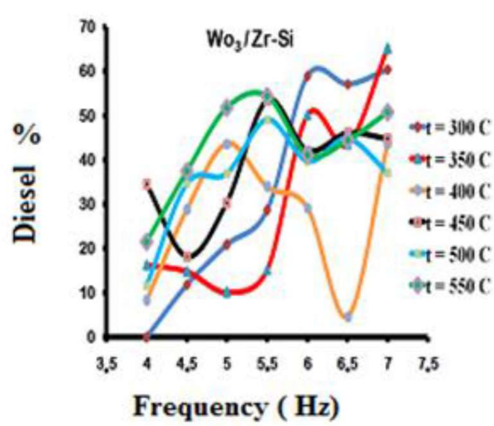

Fig.(8) Comparison of variation curves for the diesel fraction (%) vs. frequency of vibration (Hz)for catalyst WO_3/Si-Zr

At high temperatures (450-550^{0}C) the Catalyst WO_3/Si-Zr, showed a maximum output of the diesel fraction at an optimum frequency of MCA 5.5 Hz .For temperatures of 300-350C^o there was an increased frequency MCA of 7 Hz which led to an increase in output of the diesel fraction. This kind of dependence additionally confirms the theory about the interchanged influence that exist between temperature and frequency MCA on catalyst activity in conditions of aerosol nanocatalysis.The possible application of low temperatures and high frequencies MCA is promising for the working off of technological regimes of cracking aerosol nanocatalysis.In which there will be an achievement of maximum outputs of the diesel fraction.

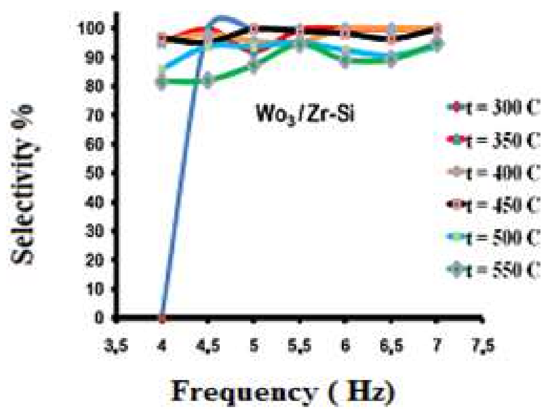

Fig. (9) Comparison of curves on the selectivity process of cracking, for light products vs. frequencies MCA for the catalyst WO_3/Si-Zr

the Catalyst (A) WO_3/Si-Zr showed higher selectivity for light oil products .In all parameters, it retained the selectivity above 80%.The best results for selectivity was achieved in 300^{0}C,by ranging from frequencies MCA of 4 Hz, the selectivity exceeded 95%.

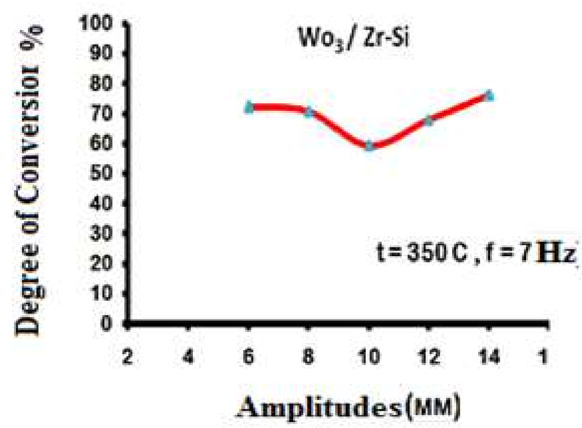

Fig.(10) Comparison of variation curves for the conversion degree (% wt) vs. amplitudes (MM) for catalyst WO_3/Si-Zr

It is established, that amplitude exerts considerably smaller effect in the degree of conversion of raw material than the frequency MCA.By varying the amplitudes for research, the Catalyst WO_3/Si-Zr managed to change the degree of conversion from 60% (A = 6 mm) to 80% (A = 14 mm). Characteristic of the curves indicates that there are some optimum amplitude MCA at which the degree of conversion will be maximized. Possibly, simultaneous varying of frequencies and amplitudes MCA may succeed to reach degree of conversion higher than 80%.

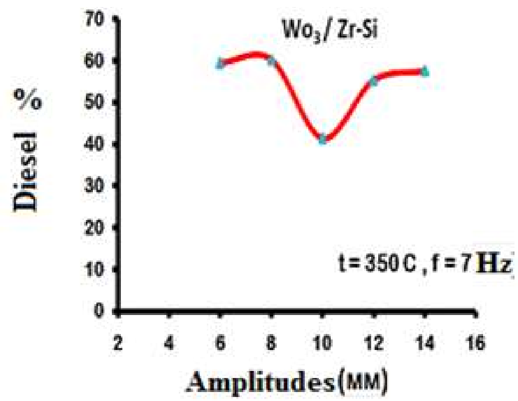

Fig.(11) Comparison of variation curves for the diesel fraction (%) vs. amplitudes MCA (MM)for catalyst WO_3/Si-Zr

The catalyst (A) WO_3/Si-Zr increase of amplitude leads to a slight change in the output of the diesel fraction an observed reverse dependence of the output of the diesel fraction increases with increasing the temperature. If for the Catalyst (A) WO_3/Si-Zr the change in the amplitude from 10 to 6 mm led to increase in output of the diesel fraction (from 40% to 60%) .The maximum values of output of the diesel fraction have been achieved at 8 mm and 14 mm , and are in inversely related to outputs of gasoline fraction. Industrial technology cracking using aerosol nanocatalysis can be developed depending on market conditions, and parameters may be applied for regulating the amount of diesel fractions.

Comparison received on the experimental results of catalytic cracking (CC) for industry and for other research to the new process of AnCVB:

as seen on the table below, when using the catalyst WO_3/Si-Zr,volume of the reactor is reduced by 15 times as compared with heterogeneous catalysis, to 2.66 times - as compared with catalytic cracking in the conditions AnCVB on the catalyst Nexus-345p and to1.94 times in conditions AnCVB for the catalyst zeolite CaA.When comparing with other samples Si-Zr catalysts succeeded to increase degree of conversion to 1.2% (sample 2) and to 10.6% (sample 1) while maintaining the selectivities in light products at the level 100%.Also WO_3/Si-Zr catalyst practically succeeded to reduce the process temperature by 2 times, as compared with the industry indicators and in conditions of AnCVB on the catalysts: zeolite CaA and Nexus-345p.

Table (1) of Comparison of the industrial process and AnCVB (Aerosol Nano Catalysis with Vibrating Bed)

Parameter	Technology					
	Industry	AnCVB				
Productivity ton/day	6300	6300				
1.Temperature, °C						
In reactor	640 - 525	350	300	600	630	350
In regenerator	640	Not required				
2. Catalyst	Nexus-345p	WO_3/Si-Zr	Si/Zr №1	CaA	Nexsus-345p	Si/Zr №2
Concentration of catalyst in reactor, kg/m³	300-700	$3\cdot10^{-3}$	$3\cdot10^{-3}$	$2\cdot10^{-3}$	$2\cdot10^{-3}$	$3\cdot10^{-3}$
3. constant rate of cracking, s^{-1}	-	0,25	0,18	0,17	4,41	0,2
4. Selectivity of light products, % mass:	74,9	99,9	98,7	84,5	85,2	99,9
5. Degree of conversion, % wt :	With recycle	per single pass				
	85	77,6	67	95	89,1	76,4
6. Volume of reactor m³	800	150		306	420	158
regenerator, m³	1600	Does not exist				
Amount of catalyst in the reactor, ton	350	less than $7\cdot10^{-4}$				
recharge the catalyst	0,545 kg/ ton raw material	0,04 kg/ tonraw material				
recycle of raw material	Exist	desirable		not required		

Another significant indicator is High selectivity in the conditions AnCVB to the catalyst WO_3/Si-Zr which is 99.9%wt that is at a high degree of conversion by a single pass (77.6 %mass). In industrial environments, there will be a requirement of recalculating of raw material. It should be noted, that the own research (sample WO_3/Si-Zr) showed an improvement on the technological characteristics of the cracking process as compared with samples Si-Zr of catalysts number 1 and number 2.Despite on some increased temperatures (the recommended value for sample WO_3/Si-Zr constitutes 350^0C),new modification allows implementing a process at a degree of conversion of 77.6% (sample №1 X = 67%, and in the sample №2 X = 76.4%), with preservation selectivity higher than 99.9%), this will allow in industrial conditions implementing the process of catalytic cracking aerosol **nanoCatalysis** on a new modification of the catalyst without an application of the recirculation stage of raw material.

Conculsions:

1. Possibility to obtain light products by technology AnCVB Using a new modification catalyst WO_3/Si-Zr.

2. Prospective regime for the design of industrial installation, operating on the catalyst WO_3/Si-Zr is temperature of 350^oC, frequency 7 Hz ,oscillation amplitude reactor 12-14 mm ,concentration of the catalyst 3 $g/m^3{}_{reactor}$.

3. Cracking of vacuum gas oil using aerosol nanocatalysis (for the studied catalyst samples) proceeds with the differential formation of diesel fractions (180-350 degrees Celsius). Maximum yield of diesel fractions with WO_3/Si-Zr catalyst is 70 %.

4. The yield of gasoline fraction for the samples studied catalyst is significantly lower than the yield of diesel fraction. Increasing the frequency of MCA, results in an increase of the gasoline fraction in the cracking products for all the investigated range of temperatures and frequencies MCA.

5. the WO_3/Si-Zr - Catalyst showed a higher selectivity for light oil . In the entire range of parameters, selectivity remained above 80%. The best selectivity results were achieved at 300C and MCA 4Hz frequency, selectivity in this case exceeded 95%.

6. It was found that the amplitude has a much smaller influence on the degree of conversion of raw materials than the frequency of MCA. By varying the amplitudes for the study WO_3/Si-Zr - catalyst failed to change the degree of conversion of 60% (A = 6 mm) to 80% (A = 14 mm). The nature of the curves indicates that there is a certain optimal amplitude MCA in which the degree of conversion is maximized.

7. A significant indicator is the high selectivity of the process conditions on AnCVB WO_3/Si-Zr catalyst that has 99.9 wt %. With a high degree of conversion per output (77.6 wt %). In industrial conditions it does not require recirculation of material.

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