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Experimental Investigation of a New Modified Catalysts (WO_3/Si-Zr) and (Si-Zr) for the Process of Aerosol Nanocatalysts by FCC of Residual Vacuum Distillation

Abstract-*This work aims at comparing between the a new modified catalyst WO_3/Si-Zr and catalyst Si-Zr to obtain gasoline and diesel fraction , The new theory of aerosol nanocatalysts technology was used in the cracking of gas oil by vacuum accompanied by the vibration of the layer of the catalyst system . The one of aim of the present work is to reduce the emissions of atmosphere polluting gases such as (H_2S and CO) .It is observed that this process is achieved at lower temperature compared to that conducted by industrial cracking process at 250 C^o , and lower amount of catalyst concentration in the reactor 2.38 (gm/m^3). This technique revealed that the selectivity of light products formation for the WO_3 /Si-Zr catalyst is higher than that with the Si-Zr catalyst at the new technology conditions.*

Keywords- *Fluid catalytic cracking (FCC); aerosol nanocatalysis (AnC); gasoline fraction; diesel fraction; catalyst WO_3/Si-Zr; catalyst Si-Zr .*

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1. Introduction

Oil refining and petrochemical industry plays very important role in the economy of any country. Therefore, the development of this industry and measures to improve the existing technologies are extremely important. Increasing the depth of oil refining is caused by growth of demand for motor fuels comparison with the oil production capabilities. Catalytic processes were introduced in the refinery processes since the end of the 1930ŝ. Catalytic cracking of alumina-silicate catalysts is one of the most widely used. The catalytic effect for various substances on the conversion of hydrocarbons was investigated by many words [1-3]. The catalytic cracking catalysts on alumina-silicate is one of the most common processes in the refining industry and contributes to a significant deepening of oil refining. The proportion of the catalytic cracking in the total amount of processed crude oil is very significant in some countries [4]. At the end of the 2000ŝ, Ukrainian scientists have formulated a new direction in the technology of gas-phase chemical processes, called the aerosol nanocatalysis (AnC). This process have the following distinctive features:

- The catalyst system consists of a moving dispersing material of a diameter 1- 2 mm, and of powder catalyst with the initial diameters 200 microns;
- The internal diffusion stages are excluded from the catalytic process;
- The diameters of the generated super active nanoparticles of catalyst is 8- 100 nm;
- Absence of carrier (catalyst and dispersing material in the reaction space are not integrated in a homogeneous system);
- The implementation of (in situ) continuous mechanochemical activation on the surface of catalyst by moving in solid material;
- Equal access of reactants on the active surface of catalyst.

The main specific characteristics of the new aerosol nanocatalyst vibration bed (AnCVB) technique [5] which allow to previously anticipate the improvement of the existing production parameters and to increase the effectiveness of the catalytic cracking (CC) are:

1) Increasing the reaction speed and correspondingly decreasing the residence time of raw material in the reaction zone due to the exclusion of internal diffusion stages of the process at aerosol nanocatalysis technology.

2) Possibility of using metal oxides as catalysts in amounts of 0.3-10g/$m^3_{reactor}$ instead of large quantities of current industrial catalysts on carriers that could include some additives of noble metals and this will reduce the capital and operational costs and consequently decrease product cost.

3) In pyrolysis process, using the new catalysts will lower the process temperature and reduce energy costs.

4) Technology of aerosol nanocatalysis will constantly maintain a high activity of catalyst, the formed coke will not be fixed on the active surface of the catalyst particles since the nanoparticles do not have pores and they subject to continuous mechanochemical activation; consequently it will be possible to exclude or substantially reduce the steam supply into the reaction zone since a suppression of reactions of coke formation will not be required.

5) Technology of aerosol nanocatalysis on vibrating bed has no restrictions on the residence time of material in the reaction zone that will allow approach of the products output, which is thermodynamically possible.

The objectives of this Research can be summarized as rollers:

1) Study the effects of temperature, frequencies and mechanical activation on the selectivity and yield of light oil on the modified catalyst sample WO_3/Si-Zr and its comparison with catalyst Si / Zr.

2) Determination of the temperature of the ignition catalyst WO_3/Si-Zr at a different mechanical activation conditions and comparing it with catalyst Si / Zr.

3)Determination of optimal conditions for carrying out catalytic cracking process on each of the catalyst system in conditions of AnCVB and the calculation of the dimensions of the main equipment for the selected regime.

4) Development of schematic technological diagrams of catalytic cracking process with application of technology aerosol nanocatalysis vibration layer of catalyst system.

The present work aims at improving the theoretical and practical basis of the aerosol nanocatalysis technology. The catalytic activity of the WO_3/Si-Zr and Si-Zr catalysis, used in the technology of aerosol nanocatalysis is vibration system with cracking of vacuum gas oil to find the gasoline - diesel fraction.

2. Test Rig Setup and Experimental Procedure

The lab. test rig layout and components are illustrated in fig.(1) The rig consists of the following components:

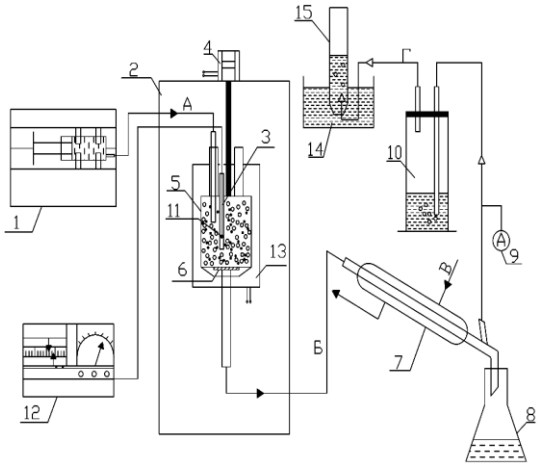


Figure 1: Illustrated diagram of the experimental setup and testing layout

1-gas oil dispenser; 2- heating chamber; 3- thermocouple well 4- vibrating device; 5 – reactor vessel 6-metallic filter ;7- condenser; 8- reaction liquid products accumulator; 9-gas fraction selector; 10– gas washer; 11 – thermocouple type (K); 12 - frequency and temperature regulator;13– electric element heating; 14 – water filled vessel; 15 – gas accumulation.

By the dispenser (1), fed vacuum gas oil to the cracking reactor (5), and was heated by the electric heater (13). The temperature inside the reactor measured from to thermocouple type K (11).the products of reaction go through the condenser (7), and entered into the receiver of liquid fraction products (8). By using vibrating device (4) the reactor is subjected to reflexive and translational motions. Aerosol nanocatalysis system (AnC) contains of a powder catalytically active material with initial particle diameters of 200 microns and dispersing solid material (dispersing material) with diameter of 1.0-1.2mm.After the end of the cracking process, taken the cracking products to the Distillation apparatus ULAB-1-42,for the analytical determination of the content gaseous reaction products using gas chromatographs: LHM-8,COLOR-500 (ethylene and hydrogen determined with accuracy not less than 0.01% vol.) [6]. Composition and octane number (research method) gasoline fraction was determined on a chromatograph CRYSTAL-5000 [7].

3. Results and Discussion

The experimental program involved a set of runs at various temperatures of the reactor, ranging from 300 ºC- 550 ºC step increase of temperature for every run, and at each temperature, the fixed reactor frequency values were charged from 4 - 7 Hz at a step increase of 0.5 Hz at successive

runs. Figure 2 shows the variation behavior of the conversion degree at various reactor temperature. It is revealed that, at 350 ºC and 7 Hz, Maximum conversion of 80 % higher was attained. The modified 1.14 times higher than the maximum degree of conversion for that with Si-Zr at a frequency 6.5 Hz. It is also observed that the reactor temperature has small influence on the rate of reaction for the catalyst WO_3/Si-Zr. Figure 2 also reveals that the variation behavior of the degree of conversion is fluctuating with the frequency at the range-selected. Moreover, slight increase with the WO^3/Si-Zr catalyst was observed over the Si-Zr catalyst at 450 ºC. It may also be noted that the maximum degree of conversion is fluctuating as the range of temperatures selected. This may be attributed to the mechanical effect of the vibration that cause a drop of the temperature at which maximum yield of the light product that is obtained at 250 ºC lower than the temperature used in the conventional industrial processes. It is also concluded from figure 2 that for Si-Zr, the reactor temperature has significant effect on the selectivity of the cracking reactions.

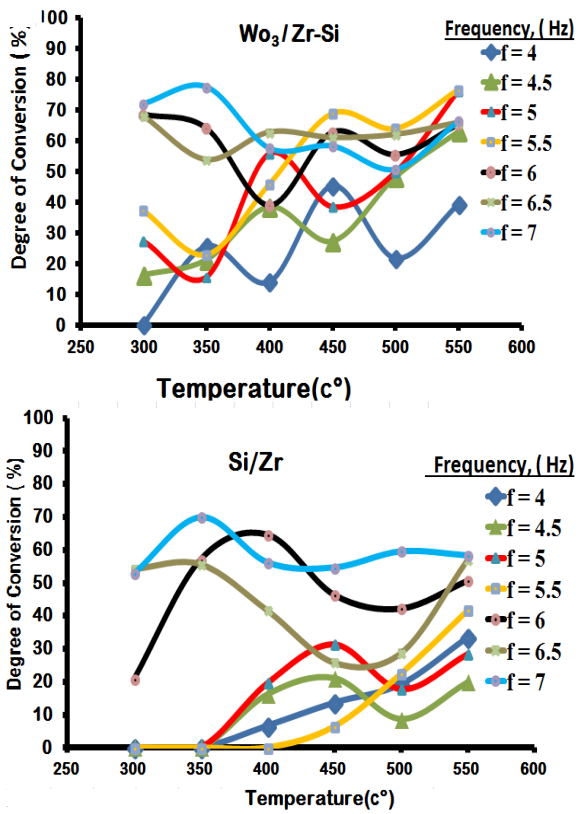


Figure 2: Variation behavior of the conversion degree with temperature for the two catalysis under research

The variation behavior of the selectivity of reactions of cracking with the reactor temperature is shown in Figure 3. Experimental results show that ,at reactor temperature of 300 ºC- 450 ºC, Light fractions above 95% is retained. At the renege of frequencies selected, expect at a frequency of 4Hz and 350ºC, where a selectivity above 95% was observed. This value of selectivity was observed to drop to 80- 85% at increased temperature of 550 ºC. For the range of parameters investigated, it is concluded that catalyst WO_3/Si-Zr has more optimized technology parameters at which a high selectivity cracking by light products achieved than catalyst Si-Zr.

Figure 4 illustrates comparison of the gasoline fraction behavior with the reactor temperature for the two catalyst under issue. The comparison shows similar behavior for both catalyst. The behavior of both catalysts was complex and strongly affected by temperature. It is found that the modified catalyst yield an output of 20 % gasoline fraction a 450 ºC and 6 Hz, compared to approximately 7 % for the catalyst Si-Zr at the same frequency.

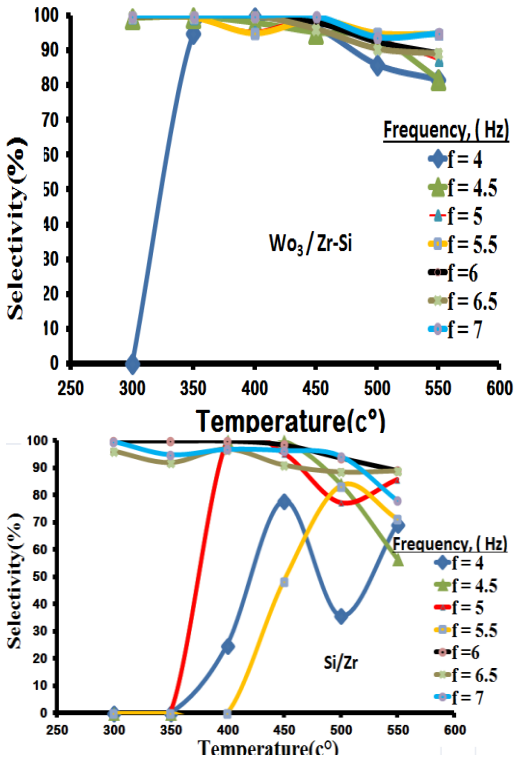


Figure 3: Variation behavior of the selectivity of the reactions of cracking with the reactor temperature for the Catalysts under issue

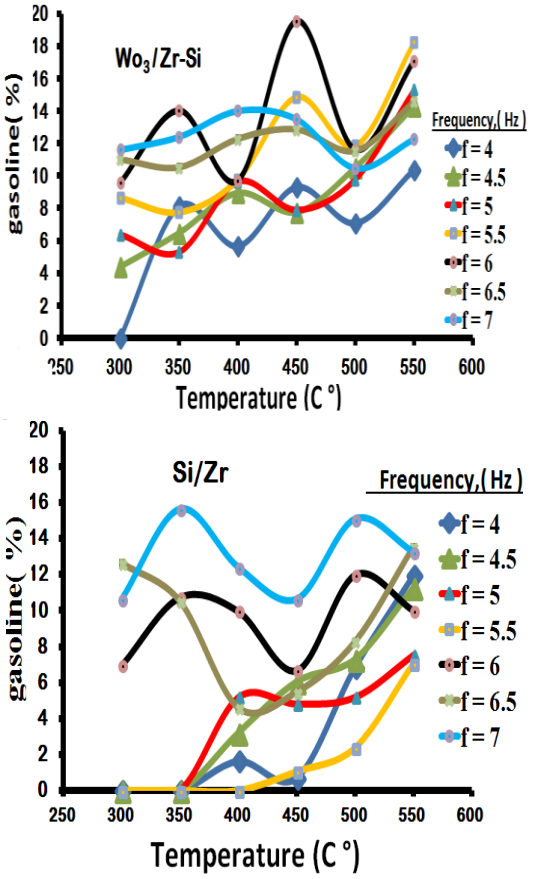


Figure 4: Variation behavior of the gasoline fraction with the reactor temperature for the two catalysis

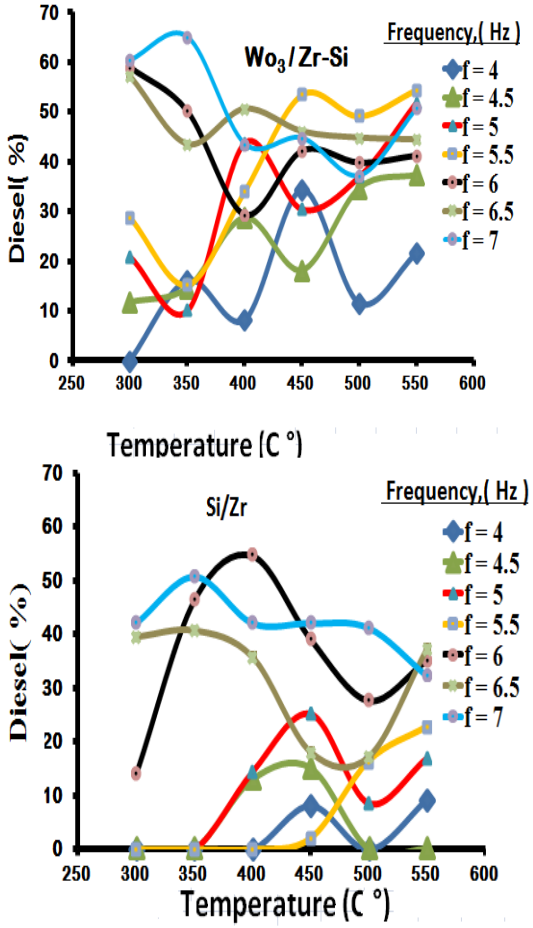


Figure 5: Variation behavior of the diesel fraction with the reactor temperature for the two catalysis

Figure 5 illustrates the variation behavior of the diesel percentage fraction with the reactor temperature of the two catalysts under issue .Results show that cracking of vacuum gas oil by aerosol nanocatalysts. For test samples at temperature range of (180 ºC -350 ºC) at which the diesel distillation occurs. Results also show that catalysts WO_3/Si-Zr resulted in a maximum output of 70% diesel fraction, compared with 60% with catalysts Si-Zr. Results also reveal that mechanical behavior dependence upon frequency and temperature of both diesel and gasoline was quite complicated. This complication may be attributed to the effect of the catalyst at variable temperature and frequencies. The vibration amplitude value also be an effect. Experimental results give the optimum combination of process condition suitable for the maximum yield of the light products (diesel and gasoline). Results also show that , with catalyst WO_3/Si-Zr , diesel fraction was maximum at 350ºC , while gasoline fraction was maximum at 450 ºC (as was show in Figure 4) .

The vibration frequency effect of frequency on the degree of conversion is shown in Figure 6 for both catalysts. The degree of frequency is observed to increase with increased vibration frequency along the range of experimental parameters. At 6Hz, approximately steady activation of the catalyst WO_3/Si-Zr surface leading to a degree of conversion of 70 %, while, for catalyst Si-Zr, steady activation achieved at 4-5.5 Hz with a lower degree of conversion of 60 %, but it was also evident by the fact, that for most reaction at a temperature of 350ºC- 500 ºC the optimum can be considered at a vibration frequency of 6Hz, here the degree of conversion reaches 70%. The Continuous increase of frequencies for most research led to a decrease in the degree of conversion. According to the influence of vibration frequency (Figure 6 and 7) for the catalytic cracking of a vacuum gasoil on the aerosol technology, nanocatalysis with greater probability can be considered for the catalyst WO_3/Si-Zr.

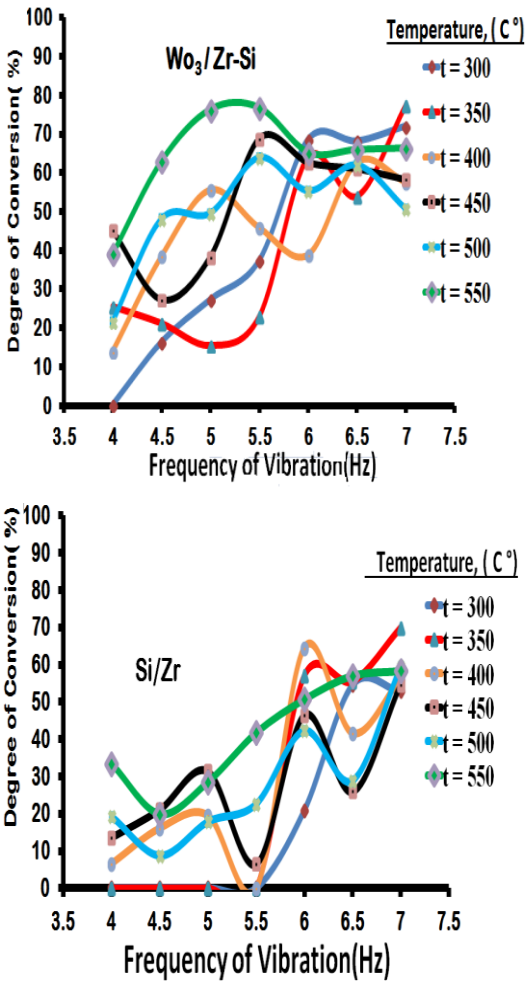


Figure 6: Variation behavior of the conversion degree with the frequency of vibration for the two catalysis

The effect of vibration frequency on the gasoline fraction with two catalysts is shown in Figure 7. It is obvious that increased frequency resulted in an increase content of gasoline fraction. This output was; however, lower than that for diesel for both catalysts within the frequency range. Maximum outputs were at temperatures of 350C°, 450C° and 550C°. However, optimum frequency value was different. It was 6 Hz for reactor temperatures of 350 °C & 450 °C, while its value dropped to 5.5Hz at 550C°. To some extent, a correlation may be assumed to exist between the reactor temperature and the vibration frequency .Where maximum yield of gasoline fraction can be achieved at lower reactor temperature. It was also observed that, depending on the reactor temperature, changing vibration frequency increased the output gasoline fraction, and that maximum diesel fraction with catalyst WO_3/Si-Zr at reactor temperatures of (450 °C-550 °C) and optimum vibration frequency of 5.5 Hz.

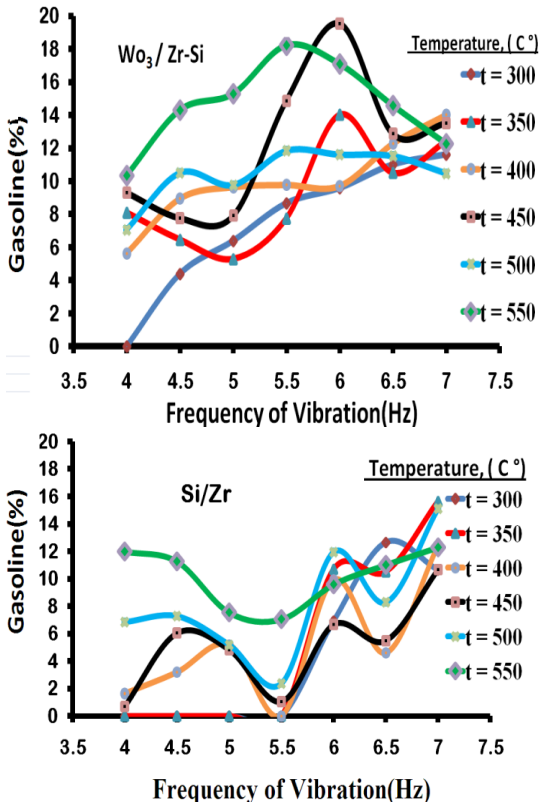
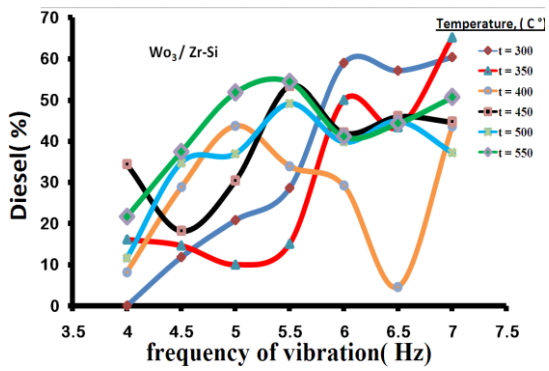


Figure 7: Variation behavior of the gasoline fraction with the frequency of vibration for the two catalysis

Figure 8 compares the effect of vibration frequency on the output diesel fraction for the two catalysts under research at the test temperature range of the reactor. The modified catalyst WO_3/Si-Zr showed maximum yield at reactor temperature of 450 °C- 550 °C and optimum vibration frequency of 5.5 Hz, while there was an increase in vibration frequency to 7 Hz at reactor temperatures of 300 °C-350 °C .This proves the hypothesis of existing mutual influence between both vibration frequency and the reactor temperature on the catalyst activity under the conditions of aerosol nanocatylsis. Low reactor temperatures and high frequencies, maximum output diesel fraction with catalyst Si-Zr where the optimum vibration frequency was 6 Hz.



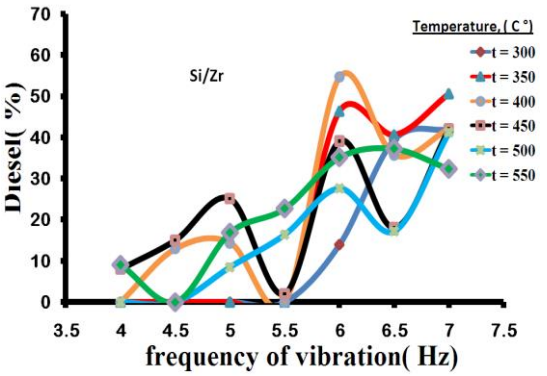


Figure 8: Variation behavior of the diesel fraction with the frequency of vibration for the two catalysis

Figure 9 compares the effect of vibration frequency on the selectivity process of cracking for the tested catalysts within the expermental range. Results show that the modified catalyst WO_3/Si-Zr have higher selectivity for both disel & gasoline than catalyst Si-Zr, where the selectivity of the modificed catalyst was above 80%. The best selectivity result was obtained at 300 °C. Also, selectivity value exceeded 90% at vibration frequency of 4 Hz. Results of catalyst Si-Zr reveated considerably greater scattering dada, that praves the great influnce of the vibration frquency on the selectivity.

The effect of mechanical vibration amplitude on the percentage weight conversion degree was also investigated, as shown in Figure 10, tests were conducted at a reactor temperature of 350 °C and a fixed frequency of 7 Hz. As compared to Figure 6, the effect vibration amplitude on the conversion degree was quits smaller than that of the vibration frequency for both catalyst. Results show that, for catalyst WO_3/Si-Zr, the conversion degree increased from 60% at amplitude of 6 mm, to 80% at 14 mm. The variation behavior of both catalysts was similar and shows an optimum value of the vibration amplitude of which there exists a maximized value of the conversion degree. In addition, more than 80% may be expected by varying both vibration amplitude and frequency simultaneously. Thus, apart from dependency selectivity of the catalyst, in conditions of aerosol nanocatalysis technology, it becomes possible to increase degree of conversion of raw materials, for example, by changing the amplitude from 8 to 14 mm.

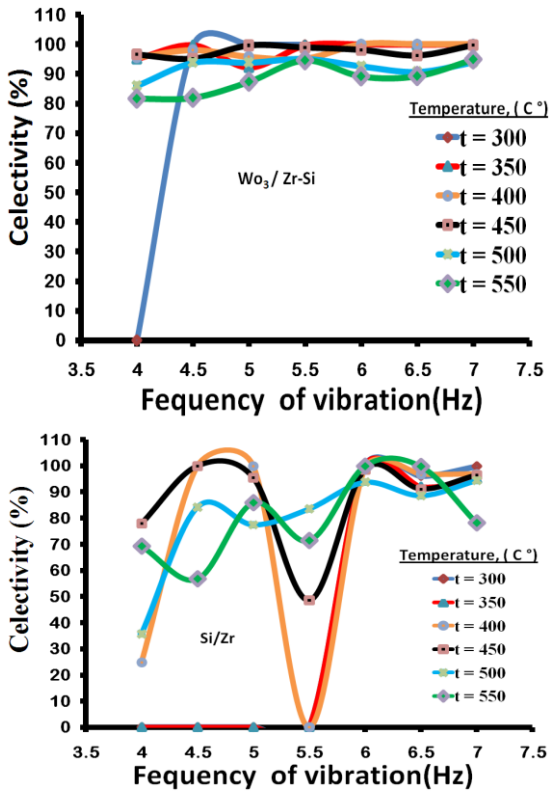


Figure 9: Variation behavior of the selectivity with the frequency of vibration for the two catalysis

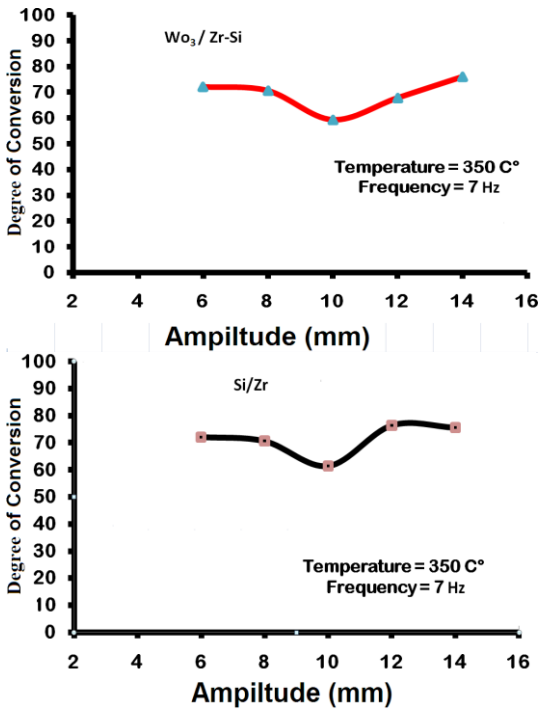


Figure 10: Variation behavior of the conversion degree with the amplitude for the two catalysis

The effect of the mechanical vibration amplitude on the output diesel fraction was also investigated. The results are shown Figure 11 at a reactor temperature of 350 °C and frequency of 7 Hz. The variation tread was almost identical with the two catalysts. However, the percentage output

of WO_3/Si-Zr changed slightly with increased amplitude. Catalyst Si-Zr the percentage output fraction was inversely dependant of increased reactor temperature. It was observed that, for catalyst WO_3/Si-Zr , increasing the amplitude from 4 to 6mm caused the output diesel fraction from 40% to 60%,and, for the Catalyst Si-Zr, increasing the amplitude from 10 to 14 mm caused an increase output from 45 to 60% .Both tested catalysts had maximum outputs at amplitudes of 8 mm and 14 mm.

Experimental results of the present work were compared with those available from the industrial catalytic cracking and other works on the new aerosol nanocatalyst vibration bed (AnCVB) process. The comparison is presented in Table 1. The comparison reveals that with catalyst WO_3/Si-Zr the reactor volume is 15 times smaller than with heterogeneous catalysis, 2.66 times with catalyst CaA zeolite. Two samples of catalyst Si-Zr caused an increase of the conversion degree by 10.6% for sample 1 and 1.2% for sample 2.Using catalyst WO_3/Si-Zr also reduced the reactor temperature by two times compared with catalysts CaA and Nexus-345p. In the AnCVB (aerosol nanocatalysis with vibrating bed) conditions, High selectivity is a significant indication of the catalyst. The selectivity for catalyst WO_3/Si-Zr is 99.9% by weight at higher degree of conversion of 77.6 % by mass in a single pass. This percentage requires recalculation for the industrial conditions. It is worth noting that catalyst WO_3/Si-Zr improved the technical characteristics of the cracking process more than catalyst Si-Zr samples, at the recommended a reactor temperature of 350°C. The new has allowed conversion degree of 77.6% (compared with 67% for sample №1, and 76.4% for sample №2) at which a process can be implemented, with a selectivity preserved at higher than 99.9%. This leads to the implementation of catalytic cracking aerosol nanocatalysis process with new modified catalyst WO_3/Si-Zr without the need to raw material recirculation stage.

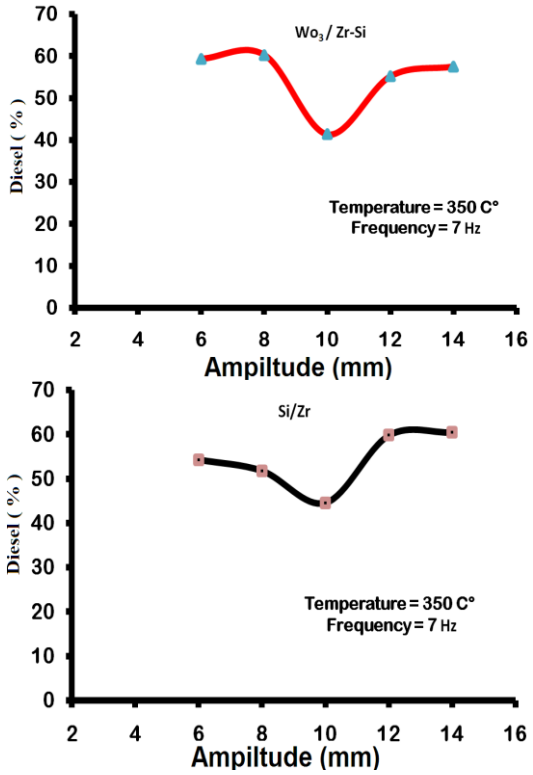


Figure 11: Variation behavior of the diesel fraction with the amplitude for the two catalysis

4. Conclusions

1) A new modification catalyst WO_3/Si-Zr and catalyst Si-Zr was tested for AnCVB technology to obtain light products.

2) Operating conditions of the process with catalyst WO_3/Si-Zr are 350°C at the reactor, 7Hz vibration frequency, 12-14mm vibration amplitude and concentration of 3g/m^3 reactor value.

3) Diesel fractions for catalyst WO_3/Si-Zr was 10 % higher than that catalyst Si-Zr in temperature range 180 °C -350 °C.

4) Increasing the vibration frequency increased the gasoline fraction for all the temperature range.

5) For both Catalysts tested, in the temperature and frequency ranges, the fraction yield of was significantly higher than that of gasoline.

6) Catalyst WO_3/Si-Zr produced higher selectivity than catalyst Si-Zr.

7) In the entire range of experimental condition selectivity was more 80 %.

8) The optimum selectivity achieved exceeded 95% at 300 °C and 4 Hz.

9) Vibration amplitude has significantly less effect on the conversion degree of raw materials than vibration frequency.

10) The conversion degree catalyst WO3 / Si – Zr varied with amplitude from 60 % at 6 mm to 80% at 14 mm.

11) Catalyst WO_3/ Si –Zr allowed a conversion degree of 77.6% with high selectivity of 99%.

Table 1: Comparison of the experimental data with the Aerosol nanocatalysis with Vibrating Bed (AnCVB) Process data

Parameter	Technology					
	Industry	AnCVB				
Productivity , ton/day	6300	6300				
1.Temperature , ºC						
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 Catalyst In reactor, Kg/m^3	300-700	$3•10^{-3}$	$3•10^{-3}$	$2•10^{-3}$	$2•10^{-3}$	$3•10^{-3}$
3. Constant rate of cracking , s^{-1}	-	0,25	0,18	0,17	4,41	0,2
4. Selectivity of light products, % мass	74,9	99,9	98,7	84,5	85,2	99,9
5.Degree of conversion,	With recycle	Per single pass				
% w	85	77, 6	67	95	89,1	76,4
6. Volume of reactor, m^3	800	150		306	420	158
Regenerator, m^3	1600	Does not exist				
Amount of catalyst in the reactor, ton	350	Less than $7•10^{-4}$				
Recharge the catalyst	0,545 Kg/ton raw material	0,04 Kg/ton raw material				
Recycle of raw material	Exist	Desirable		Not required		

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