

# Hydroconversion of Furfural Derivates on Ni-Co-Mo Catalysts

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*Hydrotreating of furfural was studied on two catalysts Ni-Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and respectively Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Catalysts characterization where performed by determining the acid strength and textural characteristics. The distribution of strength acid changes by promotion with Re. Catalyst Ni-Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed high activity on the ranges of parameters studied, and the reaction products identified are furfuryl methyl ether and oxygenate compounds recommended for addition into gasoline like tetrahydrofurfuryl-methyl ether, 2,3-dimethyl tetrahydro-furanol and 2-propyl furan. Catalyst Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had a low efficiency in the hydrogenation of furfural, the significant reaction product identified being 4-methyl-2,3-dihydrofuran.*

*Keywords: furfural, hydrogenation, catalyst, acidity, rhenium*

Concerns about the total or partial replacement of fossil fuels has been directed in recent years on the conversion of biomass in such fuels. Diminishing fossil resources, and environmental issues related to pollution with emissions of greenhouse requires valorisation of renewable resources.

Biomass produced by acid dehydrating of hemicellulose is an important intermediate for biofuels. Furfural is also a compound commonly obtained from pyrolysis of biomass. In this context, the valorization of furfural, the major product obtained by treating of natural carbohydrates, into value-added products, represents a variant for replacing of fossil fuels.

For improving stability and diminish the concentration of reactive functional groups (such as carbonyl groups and olefin), furfural must subjected to a hydrogenation process. The high reactivity of furfural in the condensation-polymerization process represents a major impediment in processes arising at relatively high temperatures such as hydrogenation reaction. The presence of acidic centers favors these condensation-oligomerization reactions, reducing the selectivity of furfural transformation. For this reason the acidic characteristics of the catalysts used in the hydrogenation of furfural is important to increase catalyst life. Thus, improving the selectivity of furfural hydrogenation process depends on the acidic centers strength of the catalyst. Also, the hydrogenation process takes place through the competitor reactions such as the aromatic ring hydrogenation, the carbonyl group hydrogenation, the carbonyl hydrogenolysis reaction etc.

The main product of the furfural hydrogenation is furfuryl alcohol (2-hydroxy dimethyl furan) and secondary byproducts typically found in literature are 2-methylfuran, 2-hydroxy-methyl-tetrahydrofuran or 2-methyl-tetrahydrofuran. For example catalytic hydrogenation of furfural was carried out in the liquid phase in the presence of a Ru /C catalyst in the temperature range of 120-200°C, using 2-propanol as the solvent. It has been found that by furfural hydrogenation was obtained furfuryl alcohol, which by hydrogenolysis leads to methyl furan, small amounts of furan and traces of tetrahydrofurfuryl alcohol. Furfuryl alcohol may dimerize or produce ether with 2-propanol. The yield of methyl furan is improved by increasing the reaction temperature and reaction time. By recycling of used Ru / C catalyst the furfural conversion decreases not

significantly and yield in furfural alcohol increases in methyl furan favor [1].

Panagiotopoulou et al. [2] tested the catalytic hydrogenation of furfural in the liquid phase over a Ru / C catalyst by hydrogen transfer. The optimal temperature was 180°C, reaction time was 10 h and as the hydrogen source was used isopropyl alcohol, thus obtaining a furfural conversion of 61%. Hydrogenation of furfural into liquid phase was carried out on a Ru catalyst deposited on Zr based support [3] or of the furfural derivatives over a catalyst based on Ni-Co-Mo [4].

The literature highlights the use and other noble metals at the catalysts preparation for furfural hydrogenation, such as like Pd [5,6], Pt nanoparticles supported [7] or Au deposited on alumina [8]. From unnnoble catalysts, the most frequently encountered in hydrogenation reaction of furfural to furfuryl alcohol are based on copper and for aromatic ring hydrogenation are used catalysts based on Ni. Thus, Villaverde Maria M. et al. [9] obtained by furfural hydrogenation at 150°C a yield of 100% in furfuryl alcohol using a Cu-Mg-Al catalyst with 40% Cu. The hydrogenation was carried out by hydrogen transfer in the liquid phase, from a solvents mixture consisting of ethanol, propanol and isopropanol.

Surpass Sitthisa et al. [10], have tested furfural hydrogenation over a Ni catalyst and one bimetallic Fe-Ni, both placed on a silica support, at a pressure of 1 bar and temperatures between 210 and 250°C. In the case of Ni catalyst, the main products obtained by hydrogenation was furfuryl alcohol and respectively, by decarbonylation was furan. These primary byproducts are converted further into other byproducts. Thus, from furan compounds are obtained C4 compounds (butane, butanal, butanol) and the alcohol is transformed mainly in 2-methylfuran, but in very small quantities. When using a Ni-Fe bimetallic catalyst increases the yield in 2-methylfuran and at the same time there is a decrease of the yield in furan respectively in C4 compounds. The addition of iron and the increasing of the amount of iron at the catalyst inhibit decarbonylating reaction and favors hydrogenation reaction of the carbonyl group.

The objective of this research is to achieve a process for hydrotreating of furfural on a catalyst Ni-Co-Mo compared

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with the same catalyst promoted with Re in order to obtain furan derivatives, components for gasoline.

## Experimental part

### Chemicals

The raw materials used in experiments were furfural p.a (Sigma-Aldrich), methanol anhydrous (Sigma-Aldrich), phosphotungstic acid hydrate (Sigma-Aldrich), cobalt (II) nitrate hexahydrate puriss p.a. (Sigma-Aldrich), nickel(II) nitrate hexahydrate puriss p.a. (Sigma-Aldrich), ammonium heptamolybdate tetrahydrate (Sigma-Aldrich), rhenium heptoxide 99.9% (Sigma-Aldrich),  $\gamma$ -alumina granulated and electrolytic hydrogen purity from Linde Company.

### Catalyst preparation

The synthesis of hydrogenation catalysts was achieved by successive impregnation with aqueous solutions of the precursors of catalysts, applying the method of filling the pores. The precursors of the catalysts are aqueous solutions of cobalt nitrate, nickel nitrate and ammonium heptamolybdate tetrahydrate at a suitable concentration according to the proposed metal content (0.8%Ni, 2% Co and 11.5%Mo for Ni-Co-Mo /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.8% Ni, 2% Co, 11.5% Mo and respectively 0.5% Re for Ni-Co-Mo-Re /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). Conditioning of the catalyst between impregnation was achieved by drying at 160°C for 4 h and the final conditioning was performed by drying at 160°C for 6 h, calcination at 450°C for 6 h and two-stage reduction by treatment with sodium borohydride in aqueous solution at a temperature of 80°C, followed by activation in a stream of hydrogen at 450°C for 6 h.

### Catalyst characterization

Chemical composition of catalysts used in the experimental program was checked by atomic absorption (Varian AA240FS). Catalysts characterization where performed by determining the acid strength and textural characteristics. The acid strength distribution of the active center has been determined by the method of thermal desorption of diethylamine using a DuPont Instruments *Thermal Analyst 2000/2100&951TGA* coupled with a module *951 Thermogravimetric Analyzer*. Textural characteristics of the catalysts (surface area, pore volume,

average pore diameter, pore-size-distribution) were determined on an Autosorb 1 Quantacrome Nova 2200 Analyzer. Texture data have been obtained by the automatic recording and processing of adsorption-desorption isotherms of nitrogen. The specific surface area was calculated using the equation in the linear part of the BET adsorption isotherm. In order to assess the distribution of pores and the pore size was used desorption branch of isotherms with hysteresis, by applying the BJH method.

### Hydrogenation of furfural

The experimental program was performed on fixed bed catalytic reactor in a continuous system. The process was carried out in isothermal conditions and the temperature was regulated with an automatic system coupled with two thermocouples fixed, placed in the reactor jacket. A metallic jacket for the mobile thermocouple was also placed in the axis of the reactor in order to measure the reaction temperature.

Reaction conditions were:

- pressure: 60 atm;
- temperature: 150-200°C;
- volume hourly space velocities of furfural (VHSV): 0.5-1 h<sup>-1</sup>;
- molar ratio hydrogen/ furfural: 10/1.

Characterization of reaction products was performed by GC-MS (Varian -3800). Operational parameters:

*GC method:* - column VF-5ms 30m X 0.25mm, ID DF=0.25;

- program of oven: temperature gradient 16°C/min up to 175°C;

- carrier gas: He;

- injector temperature: 155°C

*MS method:*

-collision cell QQQ: Flow Quench Gas (He) 2.2 mL/min; collision gas flow 1.5 mL/min;

-the electron energy: 70 eV;

-the source temperature: 230°C.

## Results and discussions

Thermodesorption curve of diethylamine for the catalysts Ni-Co-Mo /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are shown in figure 1 and 2 (A-thermodesorption from centers

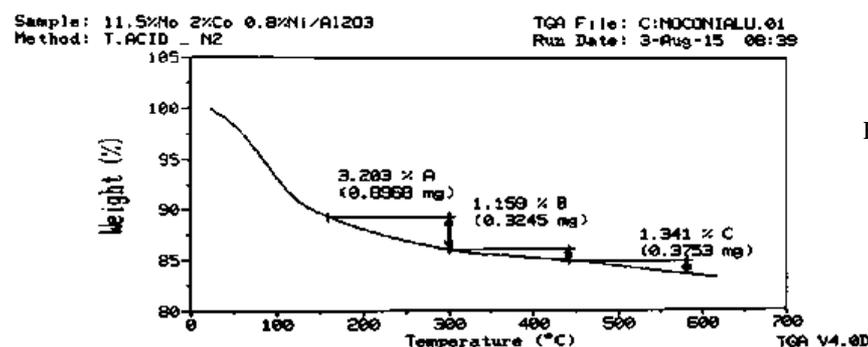


Fig. 1. Thermodesorption curve of diethylamine for the catalyst Ni-Co-Mo /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

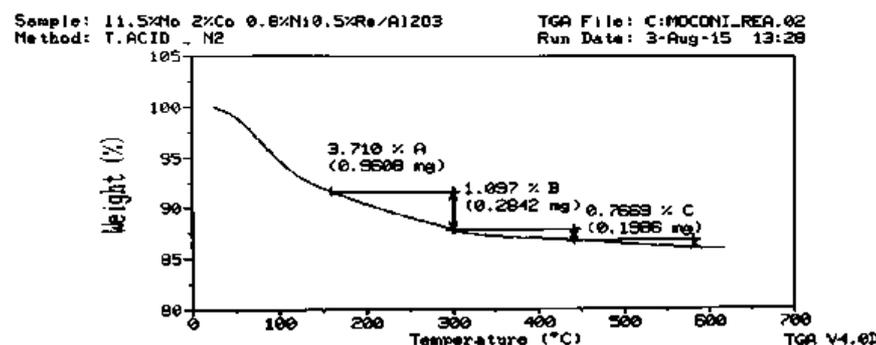


Fig. 2. Thermodesorption curve of diethylamine for the catalyst Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

The type of the acidic centers	The acidity strength, meq/g	
	Ni-Co-Mo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Ni-Co-Mo-Re/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>
Weak acids centers	0.438	0.507
Medium acids centers	0.158	0.150
Strong acids centers	0.183	0.105
Totally acids centers	0.779	0.762

**Table 1**  
THE DISTRIBUTION OF ACIDITY STRENGTH FOR THE TWO CATALYSTS

Catalyst	Specific surface area. m <sup>2</sup> /g	Pore volume. cm <sup>3</sup> /g	Medium pore diameter. nm
Ni-Co-Mo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	274.145	0.486	5.840
Ni-Co-Mo-Re/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	291.738	0.365	4.310

**Table 2**  
TEXTURAL CHARACTERISTICS OF CATALYSTS

with weakly acidic, B- thermodesorption from centers with medium acidity, C- thermodesorption from centers with high acidity).

Based on diethylamine thermodesorption curves were calculated the distribution of the acid strength for the catalysts which are presented in table 1.

From table 1 is observed that in the case of the catalyst Ni-Cr-Mo / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> acidic centers with medium acidity are found at the lowest concentration. The concentration of centers with low acidity is almost three times higher than the concentration of centers with medium acidity and the concentration of centers with high acidity is almost 16% higher than the concentration of centers with medium acidity. For the catalyst Ni-Co-Mo-Re / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> the strong acidic centers are found at the lowest concentration. The concentration of centers with low acidity is almost five times higher than the concentration centers with high acidity and the concentration of centers with medium

acidity is almost 50% higher than of the concentration centers with high acidity. The total concentration of acidic centers of the two catalysts is nearest, addition with Re causing a decrease in total acidity of the Ni-Co-Mo / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Also, after addition with Re, the distribution of strength acid changes, so strong acids centers concentration decreases with 40%, the concentration of weak acids centers increases with approx. 15% and the concentration of centers with medium acidity is close.

Textural characteristics of the two catalysts was determined by BJH method cumulative desorption pore volume, and are presented in table 2. The specific surface area of the two catalyst has a typical value for  $\gamma$ -alumina-based catalysts. After promotion with Re the pore volume and average diameter of the Mo-Co-Ni /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst decrease.

Figures 3 and 4 shows that the two catalysts possesses well-defined large pore size with monomodal pore

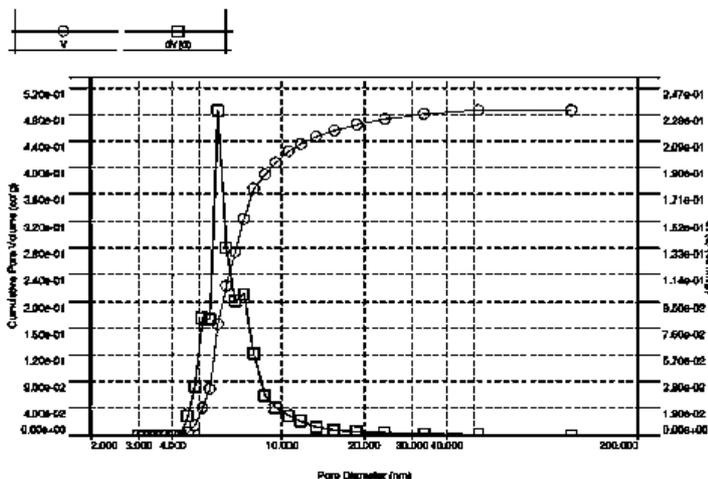
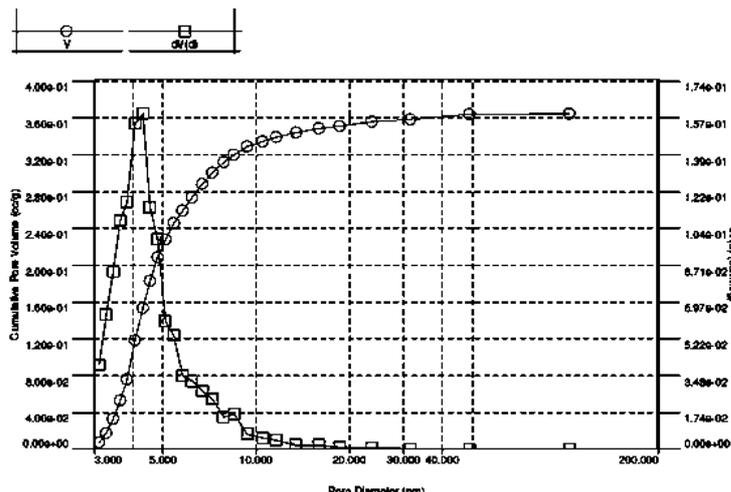


Fig. 3. The pore size distribution of the catalyst Ni-Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by BJH method desorption

Fig. 4. The pore size distribution of the catalyst Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by BJH method desorption



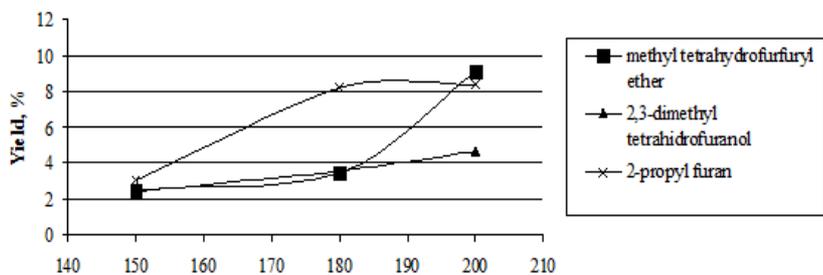


Fig. 5. Influence of temperature on yield in useful components for gasoline on the catalyst Ni-Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, at hydrogen/ furfural molar ratio of 10/1 and VHSV of 0.5 h<sup>-1</sup>

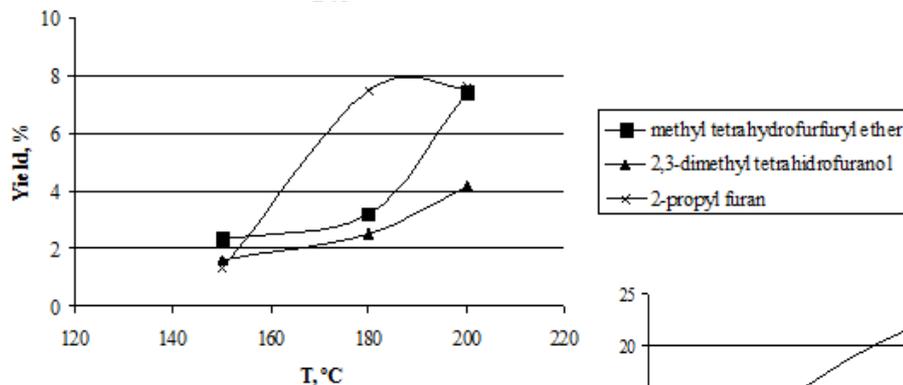
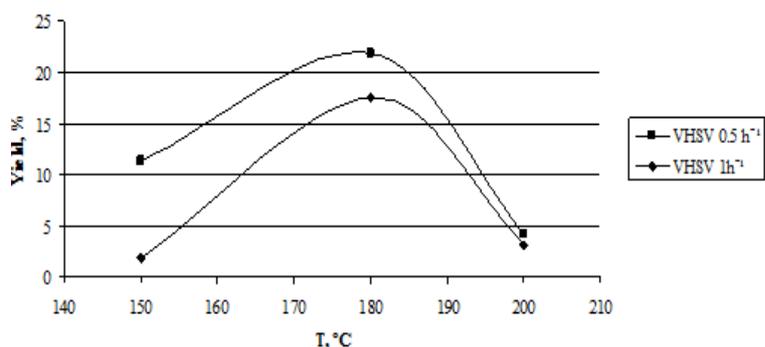


Fig. 6. Influence of temperature on yield in useful components for gasoline on the catalyst Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, at hydrogen/ furfural molar ratio of 10/1 and VHSV of 1.0 h<sup>-1</sup>

Fig. 7. Influence of temperature on yield in furfuryl methyl ether on the catalyst Ni-Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, at hydrogen/ furfural molar ratio of 10/1



structure and a maximum distribution centered around 43Å for catalyst Mo-Co-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and around 58Å for catalyst Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Catalyst Ni-Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed high activity on the ranges of parameters studied, thus the conversion of furfural is total. The reaction products identified for the catalyst Ni-Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are:

- 3-hydroxytetrahydrofuran;
- methyl tetrahydrofurfuryl ether;
- 1-propanol 2,2 dimethyl;
- furfuryl methyl ether ;
- 2,3 dimethyl tetrahydro furanol;
- 1-butanol-3-methoxy;
- 2-propyl furan.

All compounds obtained, except furfuryl methyl ether, are oxygenate stable compounds which not present the risk for the formation of gums, being recommended for addition of gasoline. The influence of temperature at different volume hourly space velocities on yield of oxygenated compounds which were obtained at concentrations of practical interest (tetrahydrofurfuryl methyl ether, 2,3-dimethyl tetrahydro furanol and 2-propyl furan) is shown in figures 5 and 6.

In figure 5 is distinguished that the yield in the three oxygenate compounds increases with temperature. Thus, at 150-180°C, the yield in 2-propyl furan increases with a slope greater than the yield in tetrahydrofurfuryl methyl ether and in 2,3-dimethyl-tetrahydrofuranol. At 180-200°C the slope of yield in tetrahydrofurfuryl-methyl ether increases with a greater value than of yields in 2,3-dimethyl-tetrahydrofuranol and 2-propyl furan. The slope of the yield variation in 2,3-dimethyl-tetrahydrofuranol has the lowest values on the variation domain studied. It notes that increasing the temperature favors the formation of methyl tetrahydrofurfuryl ether and 2-propyl furan.

The increase of volume hourly space velocities from 0.5 h<sup>-1</sup> to 1.0 h<sup>-1</sup> does not change the shape of the yield curve

variation in the three compounds but causes a decrease in the value of yield (fig. 6).

The major compound identified at furfural hydrogenation on the catalyst Ni-Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were furfuryl-methyl ether. Thus, furfuryl methyl ether yields had values of up to 20% on the ranges of parameters studied. The variation in yield of furfuryl methyl ether with temperature is presented in figure 7. It is seen that for both volume hourly space velocities, respective 0.5 h<sup>-1</sup> and 1.0 h<sup>-1</sup>, the yield in furfuryl-methyl ether varies with temperature after a parabolic curve with a maximum situated at 180°C. Increase of the volume hourly space velocity from 0.5 h<sup>-1</sup> to 1.0 h<sup>-1</sup> reduce the highest yield in furfuryl-methyl ether with approx. 20%. Decrease of furfuryl methyl ether yield at the temperature values greater than 180°C is due to its transformation both in methyl-tetrahydrofurfuryl ether and in the condensation products (oligomers).

The significant reaction product identified for hydrogenation of furfural on the catalyst Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 4-methyl-2,3-dihydrofuran. Low efficiency of the catalyst in the hydrogenation process is due to the high reactivity of furfural in oligomerization reactions, probably because Re favoring condensation reactions of furfural to form gums. Increase of temperature from 150 to 180°C favors increase of yield in 4-methyl-2,3-dihydrofuran for both volume hourly space velocities studied. Also increase of temperature at higher value than 180°C favors decrease of the yield in 4-methyl-2,3-dihydrofuran, the slope of variation having higher values than at the values of temperature less than 180°C. Furthermore the variation slope of the yield in 4-methyl-2,3-dihydrofuran shows higher values at higher temperatures and volume hourly space velocities. Increase of the volume hourly space velocities favors decrease of the yield in 4-methyl-2,3-dihydrofuran.

Increasing of temperature lead to chemical compounds with lower oxygen content and thus with improved solubility in conventional fuels.

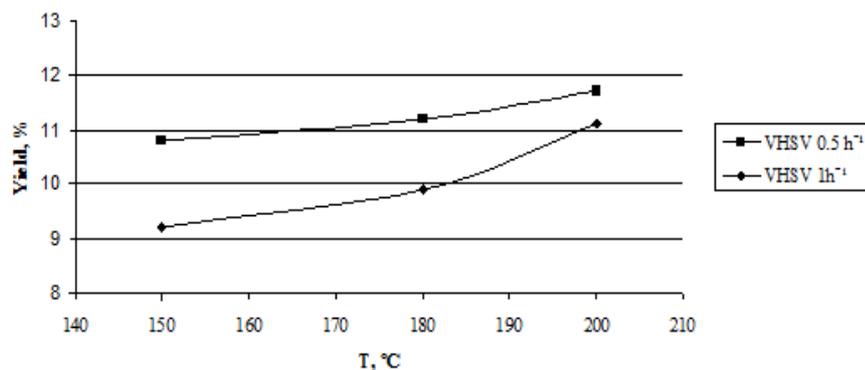


Fig. 8. Influence of temperature on yield in 4-methyl-2,3-dihydrofuran on the catalyst Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, at hydrogen/ furfural molar ratio of 10/1

## Conclusions

Hydrotreating of furfural was studied on two catalysts Ni-Co-Mo  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and respectively Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in order to obtain furan derivatives, components for gasoline. The synthesis of the catalysts was achieved by successive impregnation with aqueous solutions of the precursors of catalysts, applying the method of filling the pores. Catalysts characterization were performed by determining the acid strength and textural characteristics. The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine. Texture data have been obtained by the automatic recording and processing of adsorption-desorption isotherms of nitrogen. The experimental program was performed on fixed bed catalytic reactor in a continuous system at 60 atm, 150-200°C, volume hourly space velocities of furfural 0.5-1 h<sup>-1</sup> and molar ratio hydrogen/ furfural: 10/1. The distribution of strength acid changes by addition with Re, so strong acids centers concentration decreases with 40%, the concentration of weak acids centers increases with approx. 15% and the concentration of centers with medium acidity is close. Catalyst Ni-Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed high activity on the ranges of parameters studied, and the reaction products identified are furfuryl methyl ether and oxygenate compounds recommended for addition into gasoline like tetrahydrofurfuryl-methyl ether, 2,3-dimethyl tetrahydro-furanol and 2-propyl furan. The catalyst Ni-Co-Mo-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had a low efficiency in the hydrogenation of furfural, the significant reaction product identified being 4-methyl-2,3-dihydrofuran.

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