

## **CURRENT STATUS AND PERSPECTIVES OF DIESEL FUEL REFORMATION**

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The paper deals with the origin and the contribution of Auto/Oil - 1, the European Programme on Emissions, Fuels and Engine Technologies (EPEFE) to the understanding of the interactions between engine technologies and fuel quality in relation to their impact on exhaust emissions. The results of EPFE programme are discussed as an integrated tools to develop environmental legislation based on the cost-effective attainment of air quality targets using the best scientific and economic information.

## **AUTOMOBIL AND THE ENVIRONMENT IN THE NEXT DECADE**

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The mobility of Earth inhabitants in the mean daily transport distance of a man has increased since 1900 mainly thanks to road motor vehicles (**RMV**) from 1 km to 36 km. By year 2010 number of RMV could increase by 60 % and fuel consumption by 50 %. In Slovakia the number of passenger cars (**PC's**) could grow from today's 1060 000 on 1650 000 pieces. Legislative measures and technical achievements with respect to the environment, traffic safety, lowering of energy demands in passenger and product transport, as well as the results in fuel research (classical fuels and new ones) will contribute to significant progress in mobility and in improving the air quality.

## **PREPARATION AND HYDROTREATMENT CATALYSTS SELECTION**

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The experience of refiners over the years has revealed some limitation in hydrotreating catalysts, where there is a room for improvements and new development in hydroconversion of heavier fractions integrated into refining operation at a remarkable rate. Additives are widely used in Co and Ni promoted Mo/Al<sub>2</sub>O<sub>3</sub> catalysts to modify properties such as activity, selectivity and deactivation. Cobalt (Nikel)-molybdenum catalysts were prepared by impregnation of the same alumina carrier with certain amount of Ti (IV) clorid, and H<sub>3</sub>BO<sub>3</sub>. The results indicate that the HDS and HDN activity depends on the loading, pH of the starting selection and the method of catalyst loading. The role of additives are discussed in the light of 1H NMR spectroscopy, which confirmed that the reactions of hydrotreating are promoted. This caused the decrease of polyaromatic cores content that contained sulphur and nitrogen. Catalyst activity was analyzed in combination with two commercial catalysts (Harshaw HT-400 E, Harshaw HT-500 E) and two catalysts prepared in our laboratory: INA-123 and INA-39.

## **HYDROTREATING OF DIFFERENT PETROLEUM FRACTIONS BY LABORATORY REACTOR SIMULATION**

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The increasing market demand for improved quality fuels complies with recent environmental standards needs upgrading of petroleum fractions. The hydrotreating processes become valuable tool for quality improvement. The subject of this paper is a study of the possibility of hydrotreating two mixtures of LCO:LGO, as well as jet fuel, on CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst C-20. Using continuous laboratory reactor simulation, the aim was to find the optimum temperature for total sulphur and mercaptane sulphur removal.

## **Development of a paraffin alkylation process using zeolites in a slurry reactor**

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Alkylation of isobutane with light olefins, like butenes and propylene, produces high-octane blending stock for passenger car gasoline. Today, around 10 vol.% of the world-wide gasoline is produced by alkylation. Because of the high octane number, the low vapour pressure and the absence of aromatics and sulphur, the alkylation process is gaining increasing interest in the developments for the production of reformulated gasolines. However, the current commercial processes are under pressure because of a number of safety and environmental concerns, because of the use of liquid HF and H<sub>2</sub>SO<sub>4</sub> as catalysts. Therefore, a large research effort was initiated in the development of an alkylation process based on solid acid catalysts, which is economically more attractive and intrinsically safe. At this moment, all research developments are based on immobilised liquid acid containing halogens, still offering a number of environmental and safety concerns. However, it was found that a number of zeolite catalysts possess a good activity and selectivity to high-octane product in the alkylation reaction. The main problem with these zeolites is the fast deactivation due to oligomerisation of the butenes leading to coke formation on the catalyst. The commercial application of zeolite catalysts in alkylation demands an integrated research effort in a number of disciplines, more specifically: catalyst development, reactor engineering, process development and integration. The lifetime of the zeolites is extended from minutes to hours by the use of zeolites with a high stability, like faujasites and zeolite Beta, in a slurry reactor. The stability of the zeolites is enlarged by optimisation of the acid site density and diffusion characteristics in the catalyst. The design of the slurry reactor is optimised by minimising the local olefin concentration to suppress the oligomerisation reaction. Furthermore, the catalyst regeneration by hydrogenation over noble metals in the catalyst pores is optimised. The testing of the most promising zeolite catalysts is scaled up for optimisation of the design of catalyst particles. Integration of the research results in a preliminary process design combined with a number of constraints and targets for commercial viable operation provides feedback for further development efforts. This paper covers an overview of the integrated research efforts and results within this development project. This project is a joint research project carried out by the following companies and research institutes: SINTEF (Norway), STATOIL (Norway), OMV (Austria), University of Twente (The Netherlands), CPERI (Greece) and KTI (The Netherlands) and is funded in part by the European Commission in the framework of JOULE III.

## **ENVIRONMENTALLY FRIENDLY POSSIBILITIES TO COMPENSATE OCTANE DEFICIENCY RESULTING FROM BENZENE CONTENT REDUCTION OF MOTOR GASOLINES**

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The environmentally friendly possibilities to compensate octane deficiency resulting from benzene content reduction of motor gasolines are described and critically evaluated (use of oxygenates, light alkylates, isooctane fraction, selectively hydrogenated light cracked gasolines and reformates, isomerates, etc.). Results from blending experiments with different fractions resulting from benzene saturating isomerization, MTBE and the usual gasoline blending components are discussed.

## **New potential industrial syntheses EXPLOITED carbon MONoxide of technical grade purity OR, EVEN, AS A COMPONENT OF EXHALED GASES**

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New ways of syntheses carried out over catalysts, which are not much sensitive to common catalytic poisons, *e.g.*, sulphur compounds, are reported. In comparison to reactions with synthesis gas (CO+H<sub>2</sub>) of high purity, economics of new developed processes seems to be better. Preparation of a mixture of alkanols C<sub>1</sub>-C<sub>4</sub> from synthesis gas with admixtures of hydrogen sulphide and carbonyl sulphide over a K/MoS<sub>2</sub> and MoS<sub>2</sub>.CoS catalysts is an illustration of this group of processes. A sulphur based catalytic system (sulphur or a low molar sulphur compound, basic environment and a salt of transition metal, occasionally) catalyses a reductive carbonylation and carbonylative reduction of nitrocompounds by carbon monoxide. Thus, nitroaromates are converted to arylamines with a yield higher than 95 %, in the presence of water and CO at 100-150 °C and pressure higher than 1 MPa. A catalytic efficiency of the sulphur moieties in the developed catalytic system was estimated as follows: S : CS<sub>2</sub> : H<sub>2</sub>S : COS = 1 : 1.3 : 10 : 11. A similar efficiency was observed in the carbonylative reduction of nitrofenols to aminophenols, as well as in the reductive carbonylation of nitrobenzene by CO and methanol yielding methyl-N-phenyl carbamate. When aniline was used instead of methanol in the latter process, N,N'-diphenylurea was obtained. Similarly, N,N-diethyl-N'-phenylurea was formed by the reaction of nitrobenzene, CO and diethylamine. Methyl-N-phenyl carbamate reacts with formaldehyde to dimethyl-4,4'-diphenyl carbamate, which may be decomposed at temperature higher than 240 °C to 4,4'-diphenylmethane diisocyanate, an intermediate for a preparation of polyurethanes.

**Key Words:** synthesis gas (CO+H<sub>2</sub>), thiocompounds, hydrogensulphide, carbonylsulphide, carbonylative reduction, reductive carbonylation, methyl-N-phenyl carbamate, N,N'-diphenylurea, N,N-diethyl-N'-phenylurea, diisocyanates

## **Isopropylation of biphenyl over dealuminated mordenites**

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Isopropylation of biphenyl by propylene over dealuminated mordenites was studied in the liquid phase at the temperature of 220° C and propylene pressure 0,9 MPa. 4,4'- Selectivity increased with the degree of

mordenite dealumination. The highest 4,4'- selectivity (90%) was reached with the most dealuminated tested zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio 67. The conversion of biphenyl was 62,5%. Dealumination and next impregnation of these zeolites with 10 wt. % of cerium had slightly positive effect on 4,4'- selectivity. The conversion of biphenyl was 43,4 % and 4,4'- selectivity 92,2 % for the most dealuminated mordenite catalyst. The highest conversion of biphenyl was 61,8 % for H- mordenite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio 32.

**Key Words:** biphenyl, isopropylation, mordenite

## **THE DETERMINATION OF ALDEHYDES IN EXHAUST GASES FROM COMBUSTION ENGINES**

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A modified method for determination of aldehydes in exhaust gases was described. The method utilized 2,4-dinitrophenylhydrazine (DNPH) as derivatization reagent. Collection of aldehydes was carried out using silica gel impregnated with the reagent and the final analysis was performed by RP-HPLC. Measurements of aldehydes content in undiluted exhaust gases were carried out with different combustion engines which used different fuel. The comparison of aldehyde emissions from spark-ignition gasoline, CNG, LPG powered passenger vehicles and heavy duty engine is presented in tables

## **NON-UNIFORM ACTIVITY DISTRIBUTION CATALYSTS: II. TEST OF THE CATALYST ACTIVITY**

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An experimental investigation of the catalyst activity is presented. The influence of the active phase distribution within the catalyst pellet on the catalyst performance was studied. As a model system hydrogenation of ethylene on platinum/alumina catalyst was chosen. The catalytic performance of catalyst with various active phase distribution prepared by competitive adsorption was tested in order to estimate the optimal activity distribution for ethylene conversion.

## **CAPILLARY GAS ADSORPTION CHROMATOGRAPHY**

*by V.G. Berezkin and J. de Zeeuw*

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