

ROLE OF HYDROPROCESSING IN MODERN REFINERY

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Hydroprocessing includes hydrotreating and hydrocracking technologies. Both of these play an essential role in today's refinery and are the key technologies for production of clean, environmentally acceptable fuels, namely gasoline, jet fuel, diesel fuel and fuel oil. These technologies are also used to upgrade various refinery streams to produce high quality feedstocks for FCC and delayed cokers, as well as for production of lube stocks and petrochemicals. This paper describes all major hydrotreating and hydrocracking processes and how they fit in a modern refinery. **Key words:** hydrodesulfurization, hydrodenitrogenation, aromatic saturation, demetalization, hydrocracking, Unionfining, Unicracking, RCD Unionfining

GASOLINE ADDITIVES - STATUS AND DEVELOPMENT

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Multifunctional additive systems in gasolines prevent the formation of deposits in the whole intake system of the engine. They provide a better driveability of the car together with a reduced gasoline consumption and lower emissions compared to non additized gasolines according to specification. None optimized gasolines without or with poor package performance can cause deficits in driveability of the car stalling (hydrocarbon adsorption in intake valve deposits), sticking of the intake valves or car bon knocking by excessive deposits in the combustion chamber. Main active Components in gasoline packages are polyisobuteneamine detergents as surface active materials. Polyisobutene- monoamine on the basis of highly reactive PIB (Polyisobutene) fulfills all present requirements of a high performance detergent. We at BASF have supported the oil industry by being involved in the development of additives from the very beginning. We have followed these developments from the first generation to today's fourth generation of additives and looking forward to new regulations worldwide, starting in the next century. **Key words:** gasoline additives, valve deposits, polyisobutene

LATEST TECHNOLOGY GASOLINE DETERGENT ADDITIVE

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With the advent of stringent emission regulations and fuel economy targets, engine designs are becoming more advanced. As engine fuel efficiency is increased this generally leads to the emerging trend of hotter inlet valves. Further the modern port fuel injected engine tends to have smaller inlet valves, which provide less heat transfer area and therefore should be hotter compared to vehicles of the past. Maximum inlet valve tulip temperatures vary in engine tests and on the road. Some small modern single point fuel injection engines have been shown to manifest a maximum inlet valve temperature ranging from 300 to 400 °C depending on the cycle. Different types of gasoline detergents can be used to control deposits throughout the fuel inlet system across a range of engine designs. But it is important that these detergents possess sufficient thermal stability to ensure maintenance of inlet valve cleanliness for vehicles representative of modern European technology under all conditions. This paper examines the performance of a new

technology gasoline detergent additive (DC X) in a series of engine and laboratory tests. DC X performs very effectively in the conventional inlet valve deposit tests where the maximum temperature reached is only 250 to 260 °C i.e M102E, Opel Kadett. It also passes the standard industry no harm tests. Compared to the conventional polybutene amine and polyether amine type additives, it has an increased thermal stability proven by thermogravimetric analysis . This enhanced thermal stability translates to its highly effective performance on the hot valve single point throttle-body fuel injection VW Polo engine test under a cycle where the tulip temperature reaches 350 °C. **Key words:** detergent additive, laboratory tests, emissions

DEPOSIT CONTROL ADDITIVES FOR FUTURE GASOLINES - A GLOBAL PERSPECTIVE

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Deposit control additives are an extremely important factor in completing the vital match between today's advanced engines and gasolines. Without these powerful chemicals, carbonaceous deposits would form in precision fuel metering devices and throughout the engine's induction system to impair driveability, reduce power, increase fuel consumption, and increase exhaust emissions. Engine cleanliness is projected to become even more important in the future. Engines are evolving rapidly, providing improved performance while consuming less fuel and oil and producing fewer emissions. To satisfy these modern engines, auto manufacturers are requesting that the oil industry provide cleaner gasolines. Gasoline is also changing. Oil companies, competing in a mature industry with limited opportunities for growth, are spending huge amounts of precious capital to upgrade and modernize refineries. They must satisfy a host of regulatory requirements and consumer needs while meeting intense competition in the marketplace. Additives play a very important role. Oil companies are requesting unique, more powerful additives, with improved cost-effectiveness. Changes in both gasoline composition and engine design affect the amount and the location of engine deposits. Today's additives will work in tomorrow's gasolines. But, in the complex and challenging environment of the 90's, additives will be changing too. In the near term, we foresee customized, more powerful, and more cost-effective additive packages. They will be able to prevent and control deposits in the fuel metering and intake systems, concurrent with improved performance in the combustion chamber. Longer term, perhaps in conjunction with further changes in gasoline composition and engine design, additives will also be able to keep the combustion chamber clean, thus providing the ultimate deposit-free engine. Automobile manufacturers, oil companies, and additive companies must work together to provide the optimum solution for the ultimate customer. **Key words:** deposit control, gasoline additives, deposit formation

THE NO-HARM PERFORMANCE OF LUBRICITY ADDITIVES FOR LOW SULFUR DIESEL FUELS

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The majority of low sulphur automotive diesel fuels marketed today are treated with an additive to enhance the lubricity of the base fuel. Field experience has shown that in order to achieve the full benefits of the low sulphur diesel fuel, the lubricity additive must not only provide sufficient lubricity performance to protect sensitive diesel fuel pumps but must have no undesirable side effects. These potential side effects include: 1) degrading the properties of the base fuel, 2) interacting with crankcase lubricating oils, 3) reducing the effects of other fuel additives present. The oil and additive industries have developed a wide

range of tests to evaluate the no-harm performance of lubricity additive packages and components. This paper describes many of these tests with reference to their use in developing a novel lubricity additive package recently developed for City Diesel Fuel. **Key words:** lubricity additives, diesel fuels, lubricity performance, additive stability

SYNTHESIS AND PHYSICOCHEMICAL METHODS OF REFINING POLYOLESTER BASE OILS

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Results of research into the utilisation of waste carboxylic acids from the catalytic oxidation of cyklohexane as a stock for the production of polyolester base oils are presented in this paper. The proposed method of purifying the waste acids consists in distillation in the presence of a small addition of sulphuric acid (0.5%). Trimethylolpropane and pentaerythritol were esterified with the obtained mixture of carboxylic acids C4-C6 whereby oil bases corresponding to viscosity grades ISO10 and ISO2 2 and characterised by very low temperatures of pour point and high viscosity index were obtained. In addition, the possibility of removing unreacted carboxylic acids from esterification products in a process consisting of the technological operations: neutralisation with calcium hydroxide, dehydration and filtration was tested experimentally. It has been established that low temperature and short duration of neutralisation prevent the undesirable hydrolytic cleavage of the tested polyolesters during neutralisation. **Key words:** polyester base oils, esterification, trimethylolpropane, trimethylolpropane

HEXADECANE - HEPTANE COPYROLYSIS

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Two mixtures of hexadecane with heptane in the weight ratio 1:1 (mixture I) and 1:3 (mixture II) were pyrolysed at temperatures from 700 to 780 °C in stainless steel flow reactor in the presence of steam (H₂O : HC = 3:1 wt). Pyrolysis of pure heptane was studied in identical conditions with the aim to determine component influence on kinetics and product distribution during copyrolysis. The rate constants of heptane decomposition in both mixtures are in the entire temperature range lower than in the case of pure heptane pyrolysis. On the other hand, the present heptane accelerates hexadecane decomposition. The pyrolysis of individual heptane proceeds with the activation energy of 205 kJ mol⁻¹, however no essential change of the activation energy at copyrolysis (mixture I - 220 kJmol⁻¹, mixture II - 198 kJmol⁻¹) was observed. The same conclusion could be made on the activation energy of hexadecane in decomposition mixtures. Alkenes were prevailing in the pyrolysis products. The selectivities of ethene and propene were higher during pyrolysis of mixture I. In the range of alkane production methane and ethane were produced in larger amounts, but propane in lesser amount. A formation of secondary product - 1,3-butadiene was noted already at low temperatures and short residence times. The amount of butadiene was higher in mixture I. A difference was found between the selectivities of real products formed during copyrolysis and the selectivities calculated on the basis of their additive production from each component. The most remarkable difference is in the case of ethene: real production is higher than the additive one. The selectivities of 1-butene, 1-pentene and 1-hexene are in most cases lower than the additive ones. The formation of higher 1-alkenes (C₇ to C₁₅) and 1,3-butadiene is approximately equal to the additive

one. **Key words:** copolyrolysis, hexadecane, heptane, kinetics, pyrolysis

OXIDATION OF CYCLOHEXENE IN LIQUID PHASE OVER HYDROTALCITE-LIKE COMPOUNDS CONTAINING TRANSITION METALS

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Synthesized hydrotalcite-like compounds (HTLc) containing transition metals (Co, Mn, Ni, Cr, V) incorporated in the hydrotalcite structure were tested as catalysts of cyclohexene oxidation by oxygen in the liquid phase. The catalytic activity of these compounds was compared with corresponding transition metals in form of organic salts. The main reaction products are 2-cyclohexene-1-on and 2-cyclohexene-1-ol. The catalytic activity varies with the type of the transition metal and with incorporation of metal into the hydrotalcite structure. Solvent affects both the activity of the catalysts and product distribution. The mechanism of cyclohexene oxidation is classical free-radical and is not influenced by the mode of transition metal loading. Exception are vanadium containing HTlc, which catalyze also epoxidation of cyclohexene, which prevails over HTlc with intercalated V_2O_5 . **Key words:** cyclohexene, oxidation, hydrotalcite-like compounds, transition metals