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CATALYTIC REFORMING PROCESSES

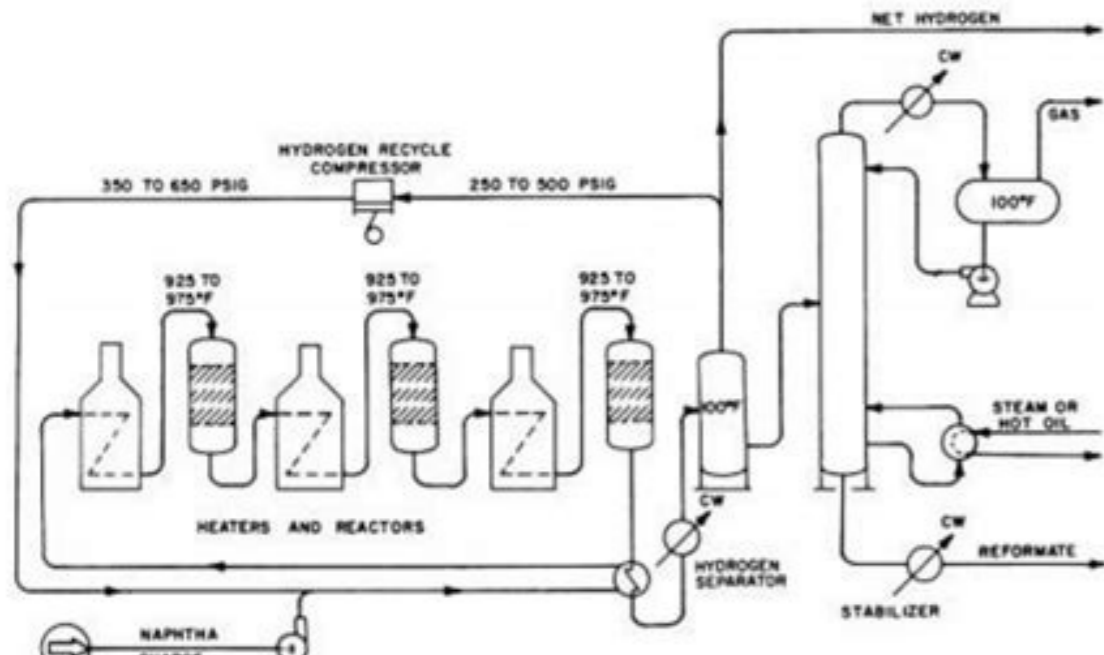
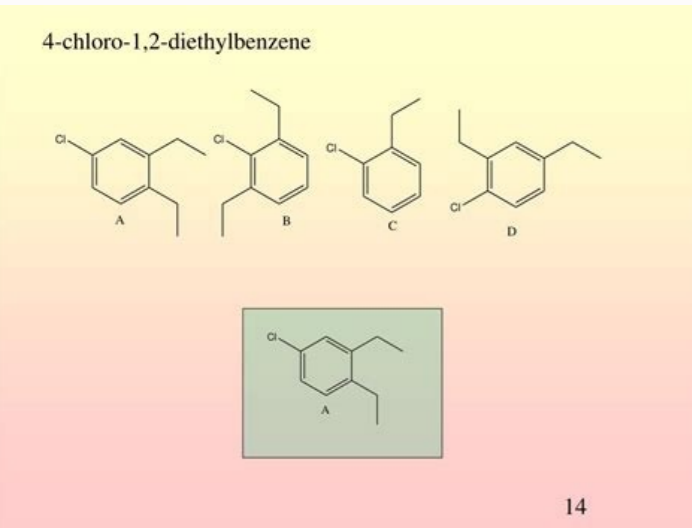


Figure 10.1 Catalytic reforming, semiregenerative process.

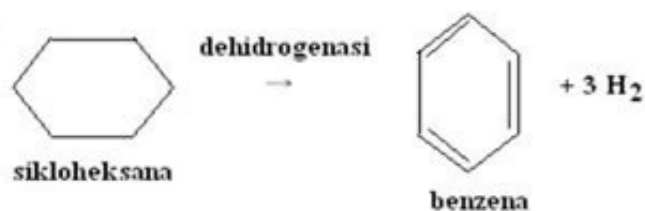
Catalytic Perfection

The quality of an engine stream depends on the quality of the reforming process. The quality of the reforming process depends on the quality of the catalyst. The quality of the catalyst depends on the quality of the reforming process. The quality of the reforming process depends on the quality of the catalyst. The quality of the catalyst depends on the quality of the reforming process.



Aromatik dengan Bahan Baku Nafta

- Hidrokarbon aromatik (BTX) dihasilkan melalui proses catalytic reforming, dengan nafta sebagai bahan baku dan katalis platina, pada suhu 450-500°C
- Reaksi pembentukan benzena :** dehidrogenasi hidrokarbon sikloparafin



Catalyst used in reforming. Catalyst used in reforming of petrol. Difference between catalytic cracking and catalytic reforming.

Full PDF PackageDownload Full PDF PackageThis PaperA short summary of this paper35 Full PDFs related to this paperDownloadPDF Pack 1 Catalytic Reforming Catalytic ReformingCatalytic reforming uses catalytic reactions to process primarily low octane heavy straight run (from the crude distillation unit) gasoline and naphtha into high octane aromatics (including benzene). Major types of reactions which occur during reforming processes : 1) dehydrogenation of naphthenes to aromatics; 2) dehydrocyclization of paraffins to aromatics; 3) isomerization; and 4) hydrocracking. Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulfur, nitrogen and metallic contaminants. In continuous reforming processes, catalysts can be regenerated one reactor at a time, once or twice per day; without disrupting the operation of the unit. 2 Catalytic Reforming 3 Catalytic Reforming 4 Catalytic Reforming 5 Catalytic Reforming 6 Catalytic Reforming 7 Catalytic Reforming 8 Catalytic Reforming 9 Catalytic Reforming 10 Catalytic Reforming 11 Catalytic Reforming 12 Catalytic Reforming 13 Catalytic Reforming 14 Catalytic Reforming 15 Catalytic Reforming 16 Catalytic Reforming 17 Catalytic Reforming 18 Catalytic Reforming 19 Catalytic Reforming 20 Catalytic Reforming 21 Catalytic Reforming 22 Catalytic Reforming 23 Catalytic Reforming 24 Catalytic Reforming 25 Catalytic Reforming 26 Catalytic Reforming 27 Catalytic Reforming 28 Catalytic Reforming 29 Catalytic Reforming SlideShare uses cookies to improve functionality and performance, and to provide you with relevant advertising. If you continue browsing the site, you agree to the use of cookies on this website. See our Privacy Policy and User Agreement for details. In the name of Allah, the Beneficial, the MercifulCATALYTIC REFORMINGKshurram ArahCONTENTS INTRODUCTION FEED STOCK REACTIONS PROCESS VARIABLES REFORMING CATALYST CATALYST CHEMISTRY VARIOUS CATALYTIC REFORMING PROCESSES CLASSIFICATION OF C.R PROCESSES UOP PLATFORMING PROCESS CATALYST REGENERATION REACTOR DESIGN CONCLUSION Q&AINTRODUCTION Demand of high-octane gasoline. 30-40 % of US gasoline production is by C.R. The production might decrease by the implementation on the aromatic content of gasoline. Only change in molecular structure so B.P of the feedstock after the process is small. C.R increases the octane of motor gasoline rather than increasing its yield. (in fact due to cracking there is a decrease in yield).FEED STOCK Feed consists of Heavy st run gasoline (HSR) Naphtha Heavy hydro cracker naphtha Naphtha containing (C6-C11) chain paraffins, olefins, naphthenes & aromatics. Aromatics in feed remains unchangedCOMPOSITION OF FEED STOCKMajor hydrocarbon groups (PONA)Paraffin Olefin Aromatics NaphthenesPONA ANALYSIS (VOL%)FEEDParaffins 30-70PRODUCT30-50OlefinsNaphthenes0-220-600-20-3Aromatics7-2045-60REACTIONS4 major reactions are categorized asDesirable Dehydrogenation of naphthenes to aromatics Dehydrocyclization of paraffins to aromatics IsomerizationUndesirable HydrocrackingDehydrogenation & Dehydrocyclization Highly endothermic Cause decrease in temperatures Highest reaction rates Aromatics formed have high B.P so end point of gasoline rises Favourable conditions High temperature Low pressure Low space velocity Low H2/HC ratio n-C7H16+ H2+ H2Isomerization Branched isomers increase octane rating Small heat effect Fairly rapid reactionsFavourable conditions High temperature Low pressure Low space velocity H2/HC ratio no significant effect+ H2Hydrocracking Exothermic reactions Slow reactions Consume hydrogen Produce light gases Lead to coking Causes are high paraffin conc feed+Favourable conditions High temperature High pressure Low space velocityPROCESS VARIABLES Catalyst type Chosen to meet refiners yield, activity and stability Temperature Primary control of changing conditions or qualities in reactor. High temp increase octane rating but decrease run length. High temp reduce catalyst stability but may be increased for declining catalyst activity. Measured in WAIT or WABT Pressure Pressure effects the reformer yield & catalyst stability. Low pressure increases yield & octane but also increases coke make. Low pressure decreases the temperature requirement for the given product qualityPROCESS VARIABLESSpace velocity Amount of Naphtha processed over a given amount of catalyst. Low space velocity favors aromatic formation but also promotes cracking. Higher space velocity allows less reaction time.H2 / HC ratio Moles of recycle hydrogen / mole of naphtha charge Recycle H2 plays a sweeping effect on the catalyst surface supplying catalyst with readily available hydrogen Increased H2 partial pressure or increasing the ratio suppresses coke formation but promotes hydrocracking.REFORMING CATALYST Catalyst used now a days is platinum on alumina base. For lower pressure stability is increased by combining rhenium with platinum. Pt serve as a catalytic site for hydrogenation and dehydrogenation reactions Chlorinated alumina provides acid site for isomerization, cyclization & hydrocracking reactions. Catalyst activity reduced by coke deposition and chlorine loss. As catalyst ages activity of the catalyst decreases so temperature is increased as to maintain the desired severity.CATALYST CHEMISTRYProperly balanced catalystMetal-Acid balance Cl Acid function CrackingMetal- Pt function Demethylation Dehydrogenation Dehydrocyclization IsomerizationVARIOUS C.R PROCESSES PLATFORMING (UOP) Powerforming (Exxon) Ultraforming (Amoco) Magnaforming (ARCO) Rheniforming (Chevron)Classification of processesContinuous Semi Regenerative CyclicUOP PLATFORMING PROCESSOctane & Temp reactors profile0.1 100 90 80 70 60 50 40 reactors 68 90 84 0.25 0.5 1 97 0 -10 -20 -30 -40 -50 -60 -70 -80 -75 reactors -30 -18 -10 0.1 0.25 0.5 1 CATALYST REGENERATION Performance of the catalyst decreases wrt time due to deactivation. Reasons for deactivationCoke formation Contamination on active sites Agglomeration Catalyst poisoning Activity could be restored if deactivation occurred because of coke formation or temporary poisons.CATALYST REGENERATION Objective of regeneration Surface area should be high Metal Pt should be highly dispersed Acidity must be at a proper level Regeneration changes by the severity of the operating conditions Coke formation can be offset for a time by increasing reaction temperatures.CATALYST REGENERATION STEPSReductionOxidationSulfate removalOxidationCarbon burnREACTOR DESIGNCONCLUSION Purpose of reforming process is to improve RONC. The basic and fastest reaction is naphthene conversion to aromatic so the feed rich in naphthene that is rich naphtha is preferred as a feed. Useful operating condition is at low pressure, low space velocity & high temperatures. The platinum is thought to serve as a catalytic site for hydrogenation & dehydrogenation reactions While chlorinated alumina as an acid site for isomerization & hydrocracking reactions. The activity of the catalyst decreases during the on stream period hence leading to regeneration.Thank YouQ&A 1 Chapter 10 Catalytic Reforming and IsomerizationThe demand of today's automobiles for high-octane gasolines has stimulated the use of catalytic reforming In catalytic reforming, the change in the boiling point of the stock passed through the unit is relatively small as the hydrocarbon molecular structures are rearranged to form higher-octane aromatics with only a minor amount of cracking. Thus catalytic reforming primarily increases the octane of motor gasoline rather than increasing its yield; in fact, there is a decrease in yield because of hydrocracking reactions which take place in the reforming operation. 2 The typical feedstocks to catalytic reformers are heavy straight-run (HSR) gasolines and naphthas (82-190°C) and heavy hydrocracker naphthas. These are composed of the four major hydrocarbon groups: paraffins, ole-fins, naphthenes, and aromatics (PONA). Typical feedstocks and reformer products have the following PONA analyses (vol %): 3 The paraffins and naphthenes undergo two types of reactions in being converted to higher octane components: cyclization and isomerization. The ease and probability of either of these occurring increases with the number of carbon atoms in the molecules and it is for this reason that only the HSR gasoline is used as reformer feed. The LSR gasoline (C5-82°C) is largely composed of lower- molecular-weight paraffins that tend to crack to butane and lighter fractions and it is not economical to process this stream in a catalytic reformer. Hydrocarbons boiling above 400°F (204°C) are easily hydrocracked and cause an excessive carbon laydown on the catalyst. 4 REACTIONS Desirable reactions in a catalytic reformer all lead to the formation of aromatics and isoparaffins as follows: Paraffins are isomerized and to some extent converted to naphthenes. The naphthenes are subsequently converted to aromatics. Olefins are saturated to form paraffins which then react as in (1). Naphthenes are converted to aromatics. Aromatics are left essentially unchanged. Reactions leading to the formation of undesirable products include: Dealkylation of side chains on naphthenes and aromatics to form butane and lighter paraffins Cracking of paraffins and naphthenes to form butane and lighter paraffins 5 As the catalyst ages, it is necessary to change the process operating conditions to maintain the reaction severity and to suppress undesired reactions There are four major reactions that take place during reforming. They are: dehydrogenation of naphthenes to aromatics dehydrocyclization of paraffins to aromatics Isomerization hydrocracking 6 Dehydrogenation ReactionsThe dehydrogenation reactions are highly endothermic and cause a decrease in temperature as the reaction progresses. In addition, the dehydrogenation reactions have the highest reaction rates of the reforming reactions which necessitates the use of the interheaters between catalyst beds to keep the mixture at sufficiently high temperatures for the reactions to proceed at practical rates The major dehydrogenation reactions are: 1. Dehydrogenation of alkylcyclohexanes to aromatics: 7. 2. Dehydroisomerization of alkylcyclopentanes to aromatics: 3. Dehydrocyclization of paraffins to aromatics: 8 The dehydrogenation of cyclohexane derivatives is a much faster reaction than either the dehydroisomerization of alkylcyclopentanes or the dehydrocyclization of paraffins, however, all three reactions take place simultaneously and are necessary to obtain the aromatic concentration needed in the reformate product to give the octane improvement needed Aromatics have a higher liquid density than paraffins or naphthenes with the same number of carbon atoms, so 1 volume of paraffins produces only 0.77 volumes of aromatics, and 1 volume of naphthenes only 0.87 volume. In addition, conversion to aromatics increases the gasoline end point because the boiling points of aromatics are higher than the boiling points of paraffins and naphthenes with the corresponding number of carbons 9 The yield of aromatics is increased byHigh temperature (increases reaction rate but adversely affects chemical equilibrium) Low pressure (shifts chemical equilibrium "to the right") Low space velocity (promotes approach to equilibrium) Low hydrogen-to-hydrocarbon mole ratios (shifts chemical equilibrium "to the right," however, a sufficient hydrogen partial pressure must be maintained to avoid excessive coke formation) 10 Isomerization ReactionsIsomerization of paraffins and cyclopentanes usually results in a lower octane product than does conversion to aromatics. However, there is a substantial increase over that of the unisomerized materials. These are fairly rapid reactions with small heat effects. 1. Isomerization of normal paraffins to isoparaffins: 11 2. Isomerization of alkylcyclopentanes to cyclohexanes, plus subsequent conversion to benzene: 12 Isomerization yield is increased by: 1. High temperature (which increases reaction rate) 2. Low space velocity 3. Low pressure Hydrocracking Reactions The hydrocracking reactions are exothermic and result in the production of lighter liquid and gas products. They are relatively slow reactions and therefore most of the hydrocracking occurs in the last section of the reactor. The major hydrocracking reactions involve the cracking and saturation of paraffins. 13 Hydrocracking yields are increased by:High temperature High pressure Low space velocity 14 Low pressure reforming is generally used for aromatics production and the following generalizations hold for feedstocks in the (68-175°C) TBP boiling range: 1. On a mole basis, naphthene conversion to aromatics is about 98% with the number of carbon atoms in the precursor being retained in the product as follows: Methylcyclopentane produces benzene. Cyclohexane produces benzene. Dimethylcyclopentane produces toluene. Dimethylcyclohexane produces xylene. Cycloheptane produces toluene. Methylcycloheptane produces xylene. 15 2. For paraffins the following number of moles of aromatics are produced from one mole of paraffins having the indicated number of carbon atoms: 16 FEED PREPARATION The active material in most catalytic reforming catalysts is platinum. Certain metals, hydrogen sulfide, ammonia, and organic nitrogen and sulfur compounds will deactivate the catalyst Feed pretreating, in the form of hydrotreating, is usually employed to remove these materials. The hydrotreater employs a cobalt- molybdenum catalyst to convert organic sulfur and nitrogen compounds to hydro- gen sulfide and ammonia, which then are removed from the system with the unreacted hydrogen. The metals in the feed are retained by the hydrotreater catalyst. Hydrogen needed for the hydrotreater is obtained from the catalytic reformer. If the boiling range of the charge stock must be changed, the feed is redistilled before being charged to the catalytic reformer. 17 CATALYTIC REFORMING PROCESSES 18 The reformer operating pressure and the hydrogen/feed ratio are compromises among obtaining maximum yields, long operating times between regeneration, and stable operation. It is usually necessary to operate at pressures from 50 to 350 psig (345-2415 kPa) and at hydrogen charge ratios of 3-8 mol H2/mol feed (2800-7600 scp/bbl). Liquid hourly space velocities in the area of 1 to 3 are in general use. The original reforming process is classified as a semiregenerative type because catalyst regeneration is infrequent and runs of 6 to 24 months between regeneration are common. In the cyclic processes, regeneration is typically performed on a 24- or 48-hour cycle, and a spare reactor is provided so that regenera- tion can be accomplished while the unit is still on-stream. Because of these extra facilities, the cyclic processes are more expensive but offer the advantages of low pressure operation and higher yields of reformate at the same severity 19 REFORMING CATALYST All of the reforming catalyst in general use today contains platinum supported on an alumina base. In most cases rhenium is combined with platinum to form a more stable catalyst which permits operation at lower pressures. Platinum is thought to serve as a catalytic site for hydrogenation and dehydrogenation reactions and chlorinated alumina provides an acid site for isomerization, cyclization, and hydrocracking reactions 20 Reforming catalyst activity is a function of surface area, pore volume, and active platinum and chlorine content. Catalyst activity is reduced during operation by coke deposition and chloride loss. In a high pressure process, up to 200 barrels of charge can be processed per pound of catalyst before regeneration is needed. The activity of the catalyst can be restored by high temperature oxidation of the carbon followed by chlorination. This type of process is referred to as semiregenerative and is able to operate for 6- to 24-month periods between regenerations. The activity of the catalyst decreases during the on-stream period and the reaction temperature is increased as the catalyst ages to maintain the desired operating severity. Normally the catalyst can be regenerated in situ at least three times before it has to be replaced and returned to the manufacturer for reclamation. 21 Catalyst for fixed-bed reactors is extruded into cylinders 1/32 to 1/16 in. (0.8 to 1.6 mm) diameter with lengths about 3/16 in. (5 mm) The catalyst for continuous units is spherical with diameters approximately 1/32 to 1/16 in. (0.8 to 1.6 mm). 22 ISOMERIZATION The octane numbers of the LSR naphtha [C5-180°F(C5-82°C)] can be improved by the use of an isomerization process to convert normal paraffins to their isomers. This results in significant octane increases as n-pentane has an unleaded (clear) RON of 61.7 and isopentane has a rating of 95 on-though isomerization where the normal and iso compounds come essentially to thermodynamic equilibrium, the unleaded RON of LSR naphtha can be increased from 70 to about 82-84. If the normal components are recycled, the resulting research octane numbers will be about 87-93 RONC. 23 Reaction temperatures of about 200-400°F (95-205°C) are preferred to higher temperatures because the equilibrium conversion to isomers is enhanced at the lower temperatures. At these relatively low temperatures a very active catalyst is necessary to provide a reasonable reaction rate. The available catalysts used for isomerization contain platinum on various bases. Some types of catalysts require the continuous addition of very small amounts of organic chlorides to maintain high catalyst activities This is converted to hydrogen chloride in the reactor, and consequently the feed to these units must be free of water and other oxygen sources in order to avoid catalyst deactivation and potential corrosion problems 24 A second type of catalyst uses a molecular sieve base and is reported to tolerate feeds saturated with water at ambient temperature. A third type of catalyst contains platinum supported on a novel metal oxide base. This catalyst has 150°F (83°C) higher activity than conventional zeolitic isomerization catalysts and can be regenerated. Catalyst life is usually three years or more with all of these catalysts. An atmosphere of hydrogen is used to minimize carbon deposits on the catalyst but hydrogen consumption is negligible 25 The composition of the reactor product can closely approach chemical equilibrium. The actual product distribution is dependent upon the type and age of the catalyst, the space velocity, and the reactor temperature. The pentane fraction of the reactor product is about 75 to 80 wt% iso-pentane, and the hexane fraction is about 86 to 90 wt% hexane isomers

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