Chapter 2. 천연가스와 석유로부터의 화학제품

• 석유화학의 기초가 되는 7가지 chemical blocks –

(1) Ethylene
(2) Propylene
(3) Butenes & Butadiene
(4) Methane
(5) Benzene
(6) Toluene
(7) Xylene

• 천연가스와 석유로부터 얻어지는 것 : olefins

(1) Ethylene
(2) Propylene
(3) Butenes & Butadiene → (olefins)

• 석유로부터 얻어진 것 – (BTX)

(5) Benzene
(6) Toluene
(7) Xylene → (Aromatic hydrocarbon)

• 천연가스로부터 얻어진 것

(4)Methane

• 석유화학(petrochemical) – petroleum 이나 natural gas 화합물 또는 이들로부터 유도된 화합물.

• 위의 7가지 chemical blocks이외에도 석유화학제품을 생산하는 중요한 원료 –

synthesis gas (syngas) : mixture of carbon monoxide(CO) and hydrogen(H_2)

• Natural gas (천연가스)

- methane을 주성분으로 한 기체성 탄화수소 혼합물 그러나 소량의 질소, CO_2, H_2S 등을 포함하고 있음.

┌ Associated gas – gas가 crude oil과 같이 존재할 경우

└ Non -associated gas – gas가 crude oil과 같이 존재하지 않을 경우

- source of energy.

• Dry natural gas – 쉽게 응축하는 탄화수소가 포함되어 있지 않은 것.

85~95%가 methane.

• Wet natural gas – 액체 찬화수소가 0.3 gal/1000ft^3 이상 포화되어

있는 것. Condensable hydrocarbon 을 제거하면 경제성이 있음.

- Dry gas 는 water content (humidity) 를 제외하고는 더 이상 treatment가 필요없음.

- Dry sour gas (or sour natural gas)는 hydrogen sulfide (H_2S)와 CO_2를 제거해야 됨. natural gas에서 acid gases 는 hydrogen sulfide와 CO_2임.

- Acid gas removal – mono and diethanolamines (MEA, DEA)이 사용됨. 또한 molecular sieve (zeolite)사용.

- Natural gas의 humidity adjustment – hydrate (powder 형태의 수산화물)의 생성을 방지하기 위하여 H_2O를 제거해야 함.

- Hydrocarbon + H_2O $\longrightarrow$ hydrate formation (under pressure and temp in gas pipe line).

- Glycol이 H_2O를 제거하는데 사용됨 –

(예) ethylene glycol, diethylene glycol등.

  - 즉, water is soluble in EG, but gas is not soluble.
  - Silica gel 이나 molecular sieve 등을 이용하여 H_2O를 제거

하기도 함.

• Wet natural gas에서 condensation hydrocarbon의 제거

- 천연 가스를 (liquid propane을 이용하여) 낮은 온도로 낮추어 제거.

• Condensable hydrocarbon (natural gas liquids)

– propane을 많이 함유하고 있는 것으로 액화시키면 liquefied petroleum gas(LPG)가 됨. LPG는 주로 propane이나 butane을 액화시킨 것.

• Natural gas는

(1)Humidity 조절

(2)Condensable hydrocarbon 제거

(3)Hydrogen sulfide, CO_2 제거하면 methane과 유사한 성분이 됨.

• Liquefied Natural gas :

천연가스가 액화되기 위해서는(상업적으로 이용되기 위해서는)

water vapor < 10 ppm

carbon dioxide < 100 ppm

H_2S < 50 ppm

• Associated gas (중동의 대부분 유전에서 발견됨)

- 대부분 oil 에는 탄화수소가스가 녹아 있으나, associated

gas는 excess gas이다.

• Natural gas liquids (NGL) – natural gas나 associated gas를 액화시킨 것.(ethane~pentane까지).

• LPG는 propane주로 이나 butane을 액화시킨 것.

• Petroleum composition and classification.

• Petroleum (crude oil)
  – natural gas, gasoline, naphtha, kerosene, fuel and lubricating oils, paraffin wax, etc.
  – nonhomogeneous mixture 이다.그러나, main은 hydrocarbon 임.(S, O_2, N_2, CH compounds) 또한, dissolved gases, metallic compound.
  – Specific한 crude oil의 성분을 아는 것이 중요한데, 이는 적절한 refinery process를 선택하기 위해서 임. 예로서 high cyclo paraffin (naphthene)을 포함하고 있는 crude oil은 ethylene을 생산하기보다는 aromatics를 생산하는데 좋음.

• 원유에(petroleum) 포함된 hydrocarbon :
  (1) 모든 원유에 포함된 hydrocarbon의 종류는 비슷함
  (2) gasoline fraction normal paraffins (straight chain)
  branched paraffins

alkyl cyclopentanes

alkyl cyclohexanes

alkyl benzenes

(3) 이사의 5종류의 gasoline fraction은 원유의 종류에 따라 비슷함.(see page9)

• Nonhydrocarbon compounds :

- Sour crude oil > {(0.05cubic feet of H_2O)/(100 gallons)}
- Crude oil의 density가 크면 클수록 sulfur (S)의 양을 많이 포함하고 있음.
- Hydrocarbon 성분으로서는 H2S,nitrogen, oxygen compounds, metallic compounds등.

• 원유(crude oil)의 classification

(1) Light Paraffinic – 비교적 낮은 wax (hydrocarbon 화합물)를 포함한 것.

(2) Paraffinic – 높은 wax와 낮은 asphalt를 포함.

(3) Naphthenic or asphaltic – 낮은 wax 와 높은 asphalt를 포함

(4) Aromatic

- 높은 aromatic 화합물을 포함.
- Mixed crude oil 은 paraffinic과 naphthenic의 중간 정도.

• The correlation Index, BMCI

(paraffinic?, mixed? or aromatic?)

BMCI(the us Bureau of Mines Correlation Index)

BMCI=48,640/K + 473.7/d – 456.8 (0 for paraffins, 100 for benzene).

여기서 K= the mid -boiling point of a fraction in Kelvin degrees.

D= the specific gravity of the fraction at 60/60 ℉

• Crude oil의 quality 결정 –

(1) specific gravity – density측정.

API (degrees) = (141.5) / (Sp. Gr. 60/60 ℉) – 131.5

(2) Pour point – oil의 흐를 때의 가장 낮은 온도 wax가 crude oil 에 얼마나 포함되어 있나?

(3) Sulfur – 양이 많으면 further treatment is needed. (corrosive and reduce the lifetime of the engine).

(4) Carbon residue – heating시 coke 발생. Do not evaporate.

(5) Ash content – amount of ash left after burning oil.

- metallic salts, metal oxide, silicon oxide

• Total World Oil Reserves – Jan.1, 1978

현재 646 billion barrels

1 barrel = 31.5 gallon = 120 l

• 표 2.2 원유증류

분급물	끓는점 영역	설명
1. 가스 메탄(65 -90%) 에탄, 프로판, 부탄	20 ℃ 이하	천연가스와 유사. 연료와 화학제품에 사용
2. 납사(경질 납사) (C_5,C_6탄화수소) 중질 납사 (C_7~C_9)	70~140 ℃ 140~200 ℃	주로 지방족과 고리지방족 화합물. 몇 가지 방향족을 포함. 가솔린의 기본물질, 벤젠은 독성이 있으므로 가솔린으로 부적합.
3. 상압gas oil 등유 디젤 연로	 175~275 ℃ 200~370 ℃	C_9~C_{16} , 제트, 트랙터, 난방 연료에 사용. 성형 C_{15}~C_{25} 화합물. 디젤과 난방 연료로 사용.
4. 중질 분급물 잔사유 (residual oil) 또는 중질 연료유	370 ℃	윤활에 사용 보일러 연료로 사용.

아스팔트 또는 “레지드”		도로, 포장등

(see 그림 2.2 also)

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◎ Refinery Processes

(석유정제반응)

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-1979년

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– steam을 이용한 thermal cracking으로 olefin을 생산하는데 주로 이용.

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ⓗ polymerization ⓘ isomerization

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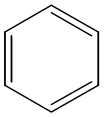

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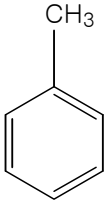

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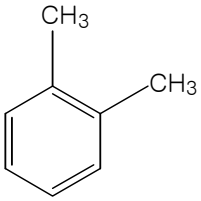

o-xylene/ m-xylene/ p-xylene

. Catalyst – the catalysts generally used for catalytic reforming. 주로 platinum 촉매 이용.

. Reforming reaction – occur at different rate and degrees of conversion depending on the themperature, hydrogen partial pressure and catalyst used.

(예) Aromatization – the dehydrogenation of cyclohexanes to benzene and methyl benzenes is completely fast and endothermic.

(ΔH = 49.08 kcal/mol)p. 60

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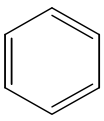

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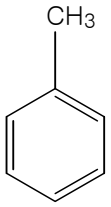

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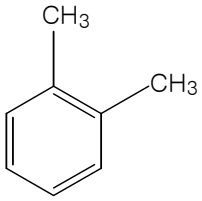

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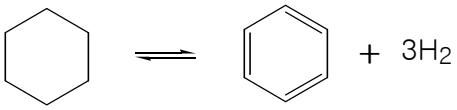


C_6H_{12} C_6H_6

- The production of benzene is favored by high temp. and low pressure.

ⓑ Hydrocracking – is a cracking reaction where by high molecular weight

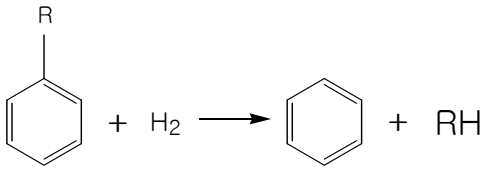
hydrocarbons pyrolyze to lower molecular weight paraffins and Olefins in the prsence of hydrogen.

. Hydrocracking is a hydrogen-consuming reaction that leads to higher gas production.

(예) $R\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3 + H_2 \rightarrow RH + CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$

ⓒ Dealkylation – like hydrocracking, is a hydrogen-consuming reaction, At higher hydrogen partial pressure, dealkylation is more favorable.

(예)



- 반응속도는 온도가 높을수록 높고, 압력은 낮을수록 yield는 높다.

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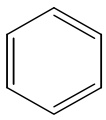

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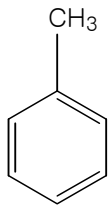

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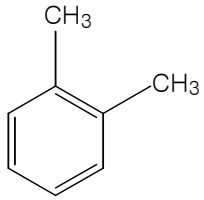

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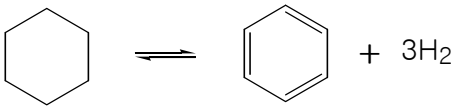

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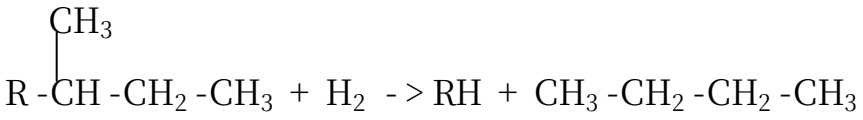

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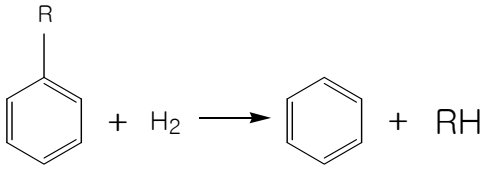

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p. 60

◎ Refinery Processes

(석유정제반응)

. Crude oil

Fuel(64%) + Petrochemical (6%)

-1979년

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ⓑ Absorption

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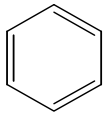

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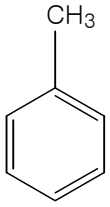

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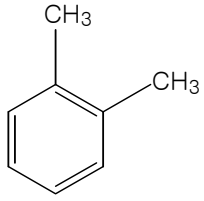

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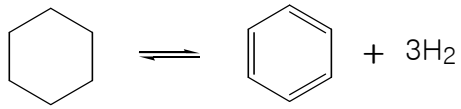

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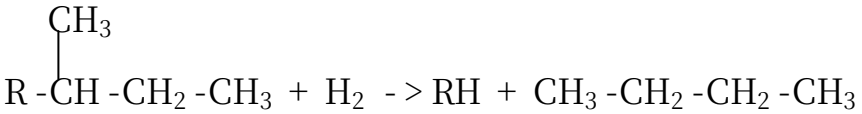

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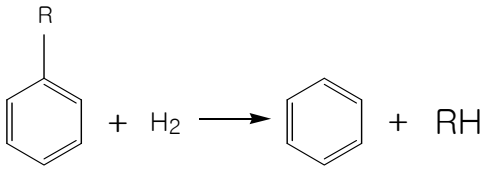

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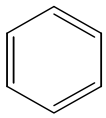

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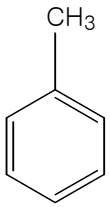

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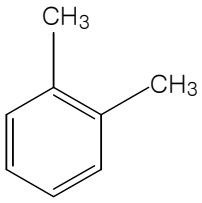

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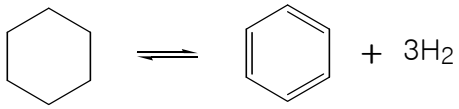

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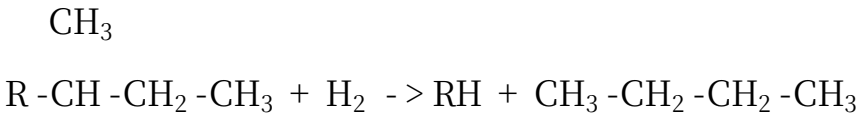

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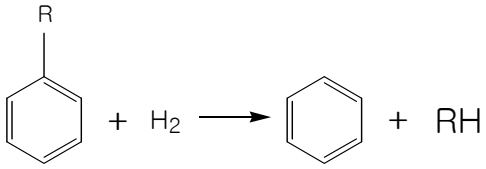

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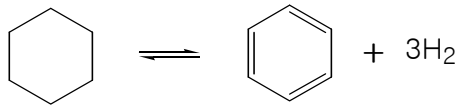

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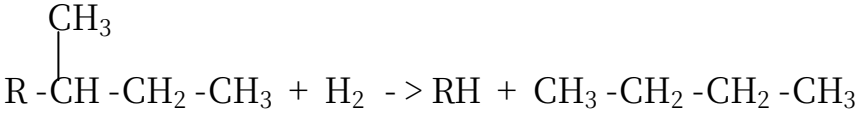

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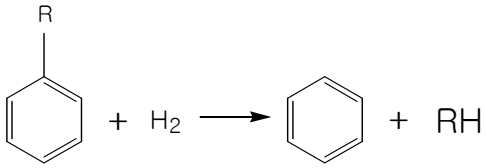

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• Hydrocracking – the most versatile modern petroleum refining processes.

- is specially adapted to the processing of low value stocks such as those that are not suitable for a catalytic cracking or reforming unit because of high metal, nitrogen and/or sulfur content.
- Is also suitable for high aromatic feeds which cannot be processed easily by conventional catalytic cracking processes.

(d) catalytic cracking – the main advantage is increased gasoline production, and the formation of hydrocarbon components having high antiknock properties. Another advantage is the production of C_3 and C_4 hydrocarbons for LCP uses.

(e) hydrogen reforming (or hydrogen treating) -
a process designed to reduce the sulfur content of atmospheric residue, vacuum gas oil, and vacuum resides.

(f) Isomerization - do not increase the quantity of gasoline but do.
Alkilation contribute to the quality of the gasoline
Dimerization

• Isomerization – a small volume but important refinery process. Normal butane is isomerized to isobutene to be used for the

alkylation of isobutylene and other olefins for the production of high octane hydrocarbons such as isooctane.

• Alkylation – generally applies to the acid catalyzed reaction between isobutene and various light olefins. The product is highly branched paraffin hydrocarbons,alkylate, used ofr blending to improve the octane number of gasoline.

• Dimerization – propylene - propane mixture to give isohexanes or propylene - butene mixture to yield isoheptenes: to upgrade the octane number. Both phosphoric acid and sulfuric acid are used as catalysts.

• Octane value

- a number indicating the degree of knocking of a fuel mixture under standard test conditions.
- Pure normal ehptane(a very high knocking fuel)is arbitrarily assigned an octane number of zero, while isooctane (a branched chain paraffin) is assigned 100. Thus a rating of 80 for a given fuel indicates that its degree of knocking in a standard test engine is equal to that of a mixture of 80 parts isooctane and 20 parts n-heptane (평균은 대략 80정도).
- lead alkyl compound (usually tetraethyl or tetramethyl

read)는 octane value가 100정도이나 공해 유발.그러므로, unleaded사용함.

• 석유 정제 반응(Petroleum Refining Reactions).

- 정제 반응의 주된 목적은 옥탄가를 높이는데 있다.

(a) 수증기 분해(steam cracking) – n-알칸,사이클로 알칸, 방향족 또는 천연가스의 에탄, 프로판, 부탄, 그리고 그 이상의 고급 탄화수소들을 에틸렌, 부텐 부타디엔으로 전환한다.

(b) 접촉분해 (catalytic cracking)- 더 큰 분자들로부터 가솔린에 적합한 탄소수 5~12의 분자들을 생산한다.

(c) 수소텀가분해 (hydrocracking) – 중질 원유를 더 휘발성이 있는 생산물로 전환함으로서 짐을 높인다. 촉매를 수소와 함께 사용하는데, 수소는 촉매상의 코크 생성을 막으며, 원치 않는 황, 질소, 그리고, 산소 화합물을, 각각 휘발성의 H_2S, NH_3, H_2O로 전환한다.

(d) 중합(polymerization, oligomerization)

저분자량 올레핀을 H_2SO_4 또는 H_3PO_4 촉매를 사용해서 연결하여 가솔린 범위의 분자로 전화한다.중합체가 아닌 소중합체(oligomers)가 생성된다.

(e) 알킬화(alkylation)

- 올레핀을 파라핀과 결합시켜 (예를 들면, 프로필렌과 이소 부탄) 가지 사슬 분자를 만든다. 황산과 불산이 촉매로 사용되며, 무연 가솔린에 있어 높은 옥탄가를 얻기 위해 대단히 중요함.

(f) 접촉 개질 (catalytic reforming)

- 직선 사슬 지방족과 고리 지방족을 백금/알루미나 또는 레늄/알루미나 촉매상에서 탈수소하여 방향족, 특히 BTX를 만든다. 미국에서 가장 널리 상용되는 정제 반응임.

(g) 탈수소 (dehydrogenation)

- 분해와 개질은 기분적으로 탈수소 반응이다. 그 밖의 탈수소 반응으로는 에틸벤젠의 styrene으로의 전환, 부텐에서 부타디엔 그리고 프로판에서 propylene으로의 전환이 있다.

(h) 이성화(dimerization)

- 직선 사슬 화합물을 가지 사슬 화합물로 전환하는 데 사용한다. 예로서 n-butane에서 isopentane, isobutane의 제조, n-butane에서 isopentane, 저비점 잡사에 있어서의 n-hexane $\longrightarrow$ isohexane, 으로 전환, n-butane $\longrightarrow$ isobutene으로의 전환등이 있다. 또한, o-,m-xylene $\longrightarrow$ p-xylene 등.

(i) 수소 첨가 처리(hydrotreating) –

석유 분급물에 있어서의, 황, 질소, 산소를 H_2S, NH_3, H_2O의 가스로 전환한다. 개질 반응 같은 다른 정제 공정으로부터 나오는 수소를 사용한다.