COVENANT UNIVERSITY
NIGERIA

TUTORIAL KIT
OMEGA SEMESTER

PROGRAMME: CHEMISTRY

COURSE: CHM 422

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1. How would you remove sulphur and salt content from crude oil?

Answer:

(i) Removal of Sulphur from Crude oil

Most sulphur compounds can be removed from petroleum streams through hydrotreating processes, where hydrogen sulphide is produced and the corresponding hydrocarbon released. Hydrogen sulphide is absorbed in a suitable absorbent and recovered as sulphur.

(ii) Desalting of Crude oil

In the desalter, water (5-15% of the volume of crude oil) is mixed with the oil at 90°C -150°C under sufficient pressure to prevent the water from vapourising at the operating temperature. The oil/water mixture is vigorously stirred to enhance intimate contact between water and the salt-containingoil. Thus, a water-oil emulsion is formed with the salts dissolving in the water. After the emulsion has settled, the lower water layer containing the dissolved salts is drained off. The process is repeated to removeasmuch salt as possible.

2. With the aid of a refinery flow diagram, show how the major processes are integrated to produce the desired petroleum fuels and nonfuel materials from crude oil.

3. Show petroleum fractions and their boiling ranges in a tabular form.

Answer:

Table 1: Petroleum Fractions and their Boiling Ranges

Petroleum Fractions	Boiling Ranges

C_1 and C_2 Gases	-162°C to -89°C
C_3 and C_4 Gases	-42°C to -1°C
Straight Run Gasoline	30°C to 75°C
Naphtha	75°C to 150°C
Heavy Naphtha	150°C to 205°C
Kerosene	205°C to 260°C
Light Gas Oil	260°C to 315°C
Heavy Gas Oil	315°C to 425°C
Lubricating Oil	about 400°C
Vacuum Gas Oil	425°C to 600°C
Residuum	> 600°C

4. Arrange the following hydrocarbons in order of their volatilities
   (i) Icosane, tetradecane, 3-ethyl-2-methylhexane, 2,6-dimethyloctane, 3, 3-diethylhexane.
   (ii) Heptane, 2, 3- Dimethylpentane, 3, 3- Dimethylpentane, 3-Ethylpentane.

5. Show the composition of natural gas, stating their category, component and amounts.

Answer:

Table 2.0: Composition of Associated Natural gas from a Petroleum Well

Category	Component	Amount (%)
Paraffinic	Methane (CH_4)	70-98
	Ethane (C_2H_6)	1-10
	Propane (C_3H_8)	Trace -5
	Butane (C_4H_{10})	Trace -2
	Pentane (C_5H_{12})	Trace -1
	Hexane(C_6H_{14})	Trace - 0.5

	Heptane and higher (C_7^+)	None- trace
Cyclic	Cyclopropane (C_3H_6)	Traces
	Cyclohexane (C_6H_{12})	Traces
Aromatic	Benzene (C_6H_6), Others	Traces
Non- hydrocarbons	Nitrogen (N_2)	Trace-15
	Carbon dioxide (CO_2)	Trace-1
	Hydrogen sulphide (H_2S)	Trace occasionally
	Helium (He)	Trace-5
	Other sulphur and nitrogen compounds	Trace occasionally
	Water (H_2O)	Trace-5

6. Diesel, kerosene, gasoline, jet fuel, or asphalt is one of the end products of the crude oil distillation and treatment process. With the aid of a flow chart discuss how any one of these

end products are formed?

7. Using suitable examples, explain the difference between cycloalkanes and alkanes with respect to volatility and heat of combustion.

Answer:

Cycloalkanes are less volatile than alkanes with the same number of carbon atoms per molecule. This is because the cycloalkanes have much larger effective surface areas than the corresponding alkanes. The larger surface areas give rise to greater Vander Waals forces interactions and hence higher boiling points. Cycloalkanes have slightly lower heats of combustion per mole than alkanes with the same number of carbon atoms. For example, heat of combustion of n-hexane is 4144 kJ/mole while that of cyclohexane is 3926 kJ/mole. This is because the cycloalkanes have lower H/C atomic ratios than the corresponding open chain structures.

8 i List out the refineries in Nigeria, stating their refining capacity, success and challenges

ii. Discuss the global distribution of petroleum resources.

9. Discuss the two main processes for the production of gasoline from refinery gases.
Answer:

Two main processes for production of gasoline from refinery gases are polymerization and alkylation. These processes increase the yield and the octane number of gasoline.

(a)Alkylation: Alkylation refers to the chemical bonding of light molecules of olefin(propylene and butylene) with isobutane to form larger branched-chain molecules (isoparaffins) that make high octane petrol. Olefins and isobutane are mixed with an acid catalyst and cooled. They react to form alkylate, plus some normal butane, isobutane and propane. The resulting liquid is neutralised and separated in a series of distillation columns. Isobutane is recycled as feed and butane and propane sold as liquid petroleum gas (LPG).

Example:

$$\text{isobutane} + \text{butylene} \xrightarrow{\text{catalyst}} \text{isooctane}$$

$$C_4H_{10} + C_4H_8 \xrightarrow{\text{catalyst}} C_8H_{18}$$

(b) Polymerisation: The process in which light unsaturated hydrocarbon molecules under pressure and temperature, over an acidic catalyst, react and combine with each other to form larger hydrocarbon molecules. Such process can be used to react butenes (olefin molecules with four carbon atoms) with iso-butane (branched paraffin molecules, or isoparaffins, with four carbon atoms) to obtain a high octane olefinic petrol blending component called polymer gasoline.

10. Discuss two treatment processes each for the light gas fraction and the residue fraction?

11. What is steam reforming?

Answer

Steam reforming refers to the reaction of a hydrocarbon feed with steam over a catalyst to

produce synthesis gas - a mixture of carbon monoxide and hydrogen.

12. Discuss the catalytic reforming process used in the petroleum industry for the production of aromatic hydrocarbons.

13. With suitable equations, highlight the production of urea.

Answer

The production of urea proceeds in two steps. The first step is the reaction of ammonia with carbon dioxide at ~180 - 215 ^{0}C and 200 to 250 atm to form ammonium carbamate. The second step involves the dehydration of the carbamate to urea.

$$2NH_3 + CO_2 \rightarrow NH_4CO_2NH_2$$

$$NH_4CO_2NH_2 \rightarrow NH_2CONH_2 + H_2O$$

14. Write the mechanism for the thermal cracking of propane.

15. Describe the production of ethanol using the indirect hydration process.

Answer

In the indirect hydration process, ethene is absorbed in concentrated sulphuric acid to form a mixture of ethyl hydrogen sulphate and diethyl sulphate. This mixture is then diluted with water whereupon the sulphates are hydrolysed to ethanol.

$$CH_2=CH_2 + H_2SO_4 \rightarrow CH_3CH_2SO_4H$$
$$CH_3CH_2SO_4H + CH_2=CH_2 \rightarrow CH_3CH_2(CH_2)_2SO_4)$$
$$CH_3CH_2SO_4H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$$
$$(CH_3CH_2)_2SO_4 + 2H_2O \rightarrow 2CH_3CH_2OH + H_2SO_4$$

The above four reaction steps can be summarised thus:

$$CH_2=CH_2 + H_2SO_4 \xrightarrow[17-35atm]{60-90\,^\circ C} CH_3CH_2SO_4H + (CH_3CH_2)_2SO_4 \xrightarrow[H_2O]{70-100\,^\circ C} 3CH_3CH_2OH + 2H_2SO_4$$

$\sim 94-98\%$ 50%

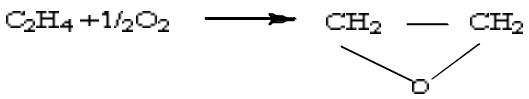
16. With the aid of a flow diagram, discuss the production of ammonia from synthesis gas.

17. Explain the formation and applications of the following:

(i) Ethylene oxide (ii) Styrene (iii) Acetone (iv) Aniline

Answer

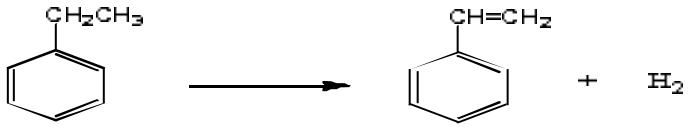
(i) The main route to ethylene oxide is oxidation of ethylene over a silver catalyst.



$\Delta H = -$ 1[illegible] $kJmol^{-1}$

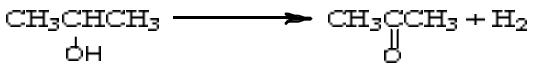
Ethylene oxide is a precursor for many important chemicals such as ethylene glycols, ethanolamines and alcohol ethoxylates. Other uses of ethylene oxide include the manufacture of poly (oxyethylene) glycols, gycol ethers and non-ionic surface active agents.

(ii) Dehydrogenation of ethyl benzene yields styrene (vinyl benzene). The most widely used catalysts for the dehydrogenation is iron oxide promoted with chromic oxide and potassium carbonate. The basic reaction is:



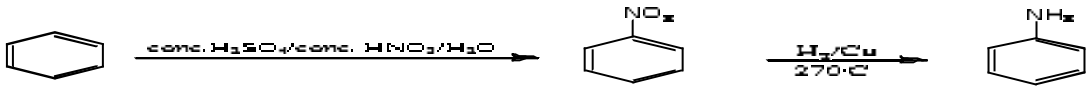
Styrene is used in the manufacture of polymers notably polystyrene and styrene butadiene rubber (SBR).

(iii) Acetone (2-propanone) is produced from the dehydrogenation of isopropyl alcohol (isopropanol) according to the equation:



Acetone is miscible with water, alcohols and many hydrocarbons hence it is a highly desirable solvent for paints, lacquers and cellulose acetate. It is also an important laboratory solvent. Acetone can be used to synthesize bisphenol A, methylisobutyl ketone, methyl methacrylate, ketene and diacetone alcohol.

(iv) Aniline is made by hydrogenation of nitrobenzene. The nitrobenzene is prepared by nitrating conc. mixture of conc. H_2SO_4, conc. HNO_3 and some water at ~50°C for 2-4 hours.



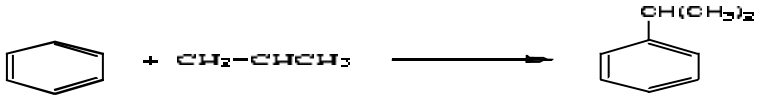
The main uses of aniline ar in the manufacture of dyestuffs, rubber, chemicals and polyurethanes (rigid foams).

18. Highlight the industrial applications of chloromethanes.

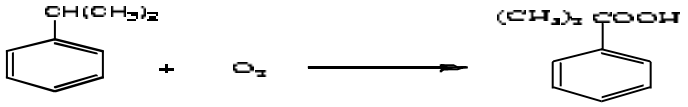
19. Discuss the manufacture of phenol through the cumene process.

Answer

The first stage is the alkylation of benzene with propylene to isopropyl benzene (cumene). Either a liquid or a gas-phase process is used for the alkylation reaction.



The second stage is the free radical oxidation of cumene to cumene hydroperoxide. The reaction conditions are approximately 100–130°C and 2–3 atmospheres in the presence of a metal salt catalyst such as Na_2CO_3.



In the third stage, the hydroperoxide is decomposed in the presence of an acid to phenol and acetone. The reaction conditions are approximately 80°C and slightly below atmospheric. Phenol and acetone are isolated from the product mixture by fractional distillation.

20. Write short notes on the properties and uses of polyethenes.