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SUMMER-19 EXAMINATION Model Answer

Subject title: Petrochemical Technology

Subject code

17651

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Important Instructions to examiners:

1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.

2) The model answer and the answer written by candidate may vary but the examiner may try

to assess the understanding level of the candidate.

3) The language errors such as grammatical, spelling errors should not be given more

Importance (Not applicable for subject English and Communication Skills.

4) While assessing figures, examiner may give credit for principal components indicated in the

figure. The figures drawn by candidate and model answer may vary. The examiner may give credit for any equivalent figure drawn.

5) Credits may be given step wise for numerical problems. In some cases, the assumed constant values may vary and there may be some difference in the candidate's answers and model answer.

6) In case of some questions credit may be given by judgement on part of examiner of relevant answer based on candidate's understanding.

7) For programming language papers, credit may be given to any other program based on equivalent concept.





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Q No.		Answer	Marking		
			scheme		
1	1 a Attempt any THREE of the following		12		
1a	i	Countries producing crude oil with their percentage share (any six)	4		
		1. Russia- 13.8% 2. United States -9%			
		3. China-5% 4. Canada- 4%			
		5. Gabon - 1% 6. Kuwait -3.5%			
		7. Ecuador - 1% 8. Libya- 1.9%			
		9. Equatorial Guinea - 1% 10. Nigeria – 2%			
		11. Qatar – 2.5 12. UAE – 4.2%			
		13. Venzuela -2.8% 14. Angola – 1%			
		15. Algeria – 1.8% 16. Iran - 4.14%			
		17. Iraq – 5% 18. Saudi Arabia-13%			
1a	ii	Reasons for considering distillation as a major unit operation in refining	4		
		process:			
		Crude oil is a mixture of hydrocarbons with different boiling temperatures. By			
		distillation it can be separated into different fractions with specified boiling			
		range. Distillation of crude takes place in two stages- First stage(atmospheric			
		distillation) and second stage (vacuum distillation)			
1a	iii	Emission control in petrochemical industries (four methods):	1 mark each		
		1. Control of emission from refinery process gases:			
		H ₂ S and mercaptans from process gases (normally used as fuel on fired heaters			
		and boilers) are removed by scrubbing the gases with an absorption solvent			
		such as aqueous amine solution.			



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	2.Control of emission from fuel combustion:			
	Emissions from fuel combustion can be controlled by changing the fue	l type		
	(switching to a cleaner fuel) or improving fuel oil quality (treating the	fuel		
	prior to combustion for removing polluting substances).			
	3. Control of emission from catalyst regeneration:			
	An external cyclone separator or electrostatic precipitator is used befor	e		
	discharging the flue gas to atmosphere. Hydrocarbons emitted are comp	pletely		
	consumed where cracking units are equipped with CO boilers.			
	4. Control of emission in storage:			
	This is achieved by the use of floating roof or pressure storage for light	-		
	hydrocarbons.			
	5. Control of emission by dispersion:			
	This is done by providing taller stacks.			
	6. Control of emission through reduction of hydrocarbon losses:			
	Hydrocarbon losses can be reduced by i) reducing flare loss ii) maximi	zation		
	of gas consumption in furnace/ boilers by proper coordination between	gas		
	producing and consuming units. iii) Installation of vapour recovery system	stem		
	while loading LPG in big wagons. iv) Proper and timely maintenance.			
	7. Sulphur recovery:			
	The classical method of sulphur recovery is the claus process. This pro-	cess is		
	based on producing elemental sulphur, by first converting $1/3$ of the H ₂	S to		
	SO_2 and using this to combine with the remaining H_2S in the presence of	of a		
	catalyst to form sulphur.			
1a iv	Chemicals derived from C1 hydrocarbon			
	1. Methanol3. Formaldehyde		¹∕₂ marl	Κ

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	2. Chloromethane 4. Methylene dichloride	each
	Chemicals derived from C2 hydrocarbon	
	1. Ethanol 3. Ethylene oxide	¹∕₂ mark
	2. Styrene 4. Acetaldehyde:	each
	(Due consideration should be given for any other chemical derived from C1	
	and C2 hydrocarbon)	
1b	Attempt any ONE of the following	06
1b i	Description of thermal cracking process:	
	Thermal cracking is a refining process in which heat ($^{\sim}800^{\circ}C$) and pressure	
	(~ 700kPa) are used to break down, rearrange hydrocarbon molecules.	2
	Visbreaking, steam cracking, coking are applications of thermal cracking.	
	Delayed coking	
	In this method the heated charge is transferred to large coke drums which	
	provide the long residence time needed to allow the cracking reactions to	2
	proceed to completion. Initially the heavy feedstock is fed to a furnace which	
	heats the residuum to high temp.(480-510°c) at low pressures (25-30 psi) and	
	is designed & controlled to prevent premature coking in the heater tubes. The	
	mixture is passed from the heater to one or more coker drums where the hot	
	materials is held for 24 hours until it cracks into lighter products. Vapours	
	from the drums are returned to a fractionator where gas, naphtha separated out.	



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	-			
	Reaction: $(CH_3)_2C = CH_2 + CH_3OH \rightarrow (CH_3)_3CO-CH_3$			
	Isobutene and methanol enters a fixed bed reactor, where 90% of butene is			
	consumed. The products are cooled to 20° C, whereby unreacted methanol and	3		
	MTBE are condensed. Butenes are separated first from the reactor mix by			
	distillation (debutanizer). Methanol and MTBE mixture is obtained from the			
	bottom of the column which is again distilled in a separate column to obtain			
	MTBE as the bottom product. The gas phase containing methanol vapours is			
	washed with water in a demethanolizer, dried, heated to about 300°C and			
	admitted to an isomerization unit where 2 and n-butene are converted into			
	isobutene. Isobutene is cooled and then recycled.			
	Attempt any FOUR of the following	16		
a	Reason for crude oil being known as black gold:			
	Crude oil is yellowish black oil that is extracted from under the surface of the			
	earth. It is one of the most necessitated worldwide required commodities. Any			
	fluctuation in the crude oil prices can have direct and indirect influence on the	2		
	economy of the countries. That is why crude oil is called black gold.			
	Advantages of crude oil over other energy sources:			
	1. It is one of the most abundant energy resources.	¹∕₂ mark		
	2. Liquid form of oil makes it easy to transport and reuse.	each for any		
	3. Oil has high heating value.	two pints		
	4. No new technology needed for use.			
	Disadvantages of crude oil over other energy sources:			
	1. Oil burning leads to carbon emission.	¹∕₂ mark		
	2. Oil recovery process not efficient enough.	each for any		
	a	Reaction: (CH ₃) ₂ C= CH ₂ + CH ₃ OH → (CH ₃) ₃ CO-CH ₃ Isobutene and methanol enters a fixed bed reactor, where 90% of butene is consumed. The products are cooled to 20°C, whereby unreacted methanol and MTBE are condensed. Butenes are separated first from the reactor mix by distillation (debutanizer). Methanol and MTBE mixture is obtained from the bottom of the column which is again distilled in a separate column to obtain MTBE as the bottom product. The gas phase containing methanol vapours is washed with water in a demethanolizer, dried, heated to about 300°C and admitted to an isomerization unit where 2 and n-butene are converted into isobutene. Isobutene is cooled and then recycled. Attempt any FOUR of the following a a Reason for crude oil being known as black gold: Crude oil is yellowish black oil that is extracted from under the surface of the earth. It is one of the most necessitated worldwide required commodities. Any fluctuation in the crude oil prices can have direct and indirect influence on the economy of the countries. That is why crude oil is called black gold. Advantages of crude oil over other energy sources: 1. It is one of the most abundant energy resources. 3. Oil has high heating value. 4. No new technology needed for use. Disadvantages of crude oil over other energy sources: 1. Oil burning leads to carbon emission. 2. Oil recovery process not efficient enough 1. Oil burning leads to carbon emission.		



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octane rating. Reforming is an	important process used to convert low	w octane 2
naphtha into high octane gase	bline blending components called ref	formates.
Reforming represents the total	effect of numerous reactions such as o	cracking,
polymerization, dehydrogenatio	n, isomerization taking place simultane	eously.
Reactions	Annall Academical Fordettern	
Hoc - CH2	$H_{C} = C_{H}$	
H ₂ C	heat HC 11 +31	10
$H = H_2 C - C H_2$	and Catalyst HC - CH	2
Methyl Cyclobexane	Toluene	
D B	CH3	(8)
CH3- CH2- CM2- CH2- CH2-	CH2-CH3 - CH3 ALOS	+ 4H2
n-Heptane	Cr2U3 ··· riz v3 V	e .
Collection Plat	2233 Lotid Correctoral	
Catalyst: Platinum		
Pressure: 15-50 atms		
Temperature: 470-525 ^o C		
OR		







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3	b	Fractions obtained from crude oil with	h their uses and l	boiling point range	1 mark each
		Fractions	Boiling	Uses	
			point range		
		1. Uncondensed gases	$< 30^{\circ}$ C	Domestic	
				fuel,	
				synthesis of	
				organic	
				chemicals.	
		2. Petroleum ether	30-70°C	Solvent for	
				fats,	
				essential	
				oils, used in	
				dry cleaning.	
		3.Gasoline or petrol or motor	40-120°C	As a motor	
		spirit		fuel for IC	
				engines,	
				solvent, in	
				dry cleaning.	
		4. Naphtha	120-180°C	As a solvent	
				and in dry	
				cleaning,	
				feed stock	
				for	
				petrochemic	
				als.	
		5. Kerosene oil	180-250°C	Illuminant,	
				fuel for	
				stoves	
		6. Diesel oil	250-320°C	Diesel	
				engine fuels,	



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				carbureting of water gas	
		7.Heavy oil On vacuum distillation of heavy oil gives lubricating oil, petroleum jelly, greases, paraffin wax etc.	320-400°C	Fuel for ships, metallurgica l furnaces, feed stock for cracking processes.	
		8.Residue	> 400°C	Used for making roads and water proofing roof, as a fuel, for moulding electrode rods.	
3	c	Manufacturing of styrene:			
		Description Reaction involved in the manufacture of 1. Alkylation of benzene $(g) + H_2C = CH_2(g) \xrightarrow{650 \text{ K}, 20 \text{ atm}}_{\text{acid catalyst}}$ benzene $C_{\theta}H_6$ ethene 2. Dehydrogenation of ethyl benzene	styrene: H ₃ C— CH ₂ (g)		







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		Explanation: 43% of world crud	de produced is shared amor	ng the gro	oup	
		members. Currently the organization	on has a total of 14 member c	ountries. 7	Гће	
		member countries are Algeria, An	ngola, Congo, Ecuador, Equat	orial Guin	nea, 3	
		Gabon, Iran, Iraq, Kuwait, Libya, N	Vigeria, Saudi Arabia, UAE, V	enezuela		
		Objectives of OPEC are				
		1. To avoid useless fluctuation in p	rices in international market.			
		2. To provide an efficient economic	c and regular supply of petrole	um to		
		consuming nations and a fair return	of capital to those investing in	petroleun	n	
		industries				
4a	ii	Characteristics of crude oil:				
		1.Crude is an yellowish black oily c	complex mixture			
		2. Flash point: below 10° C			1/	
		3. Kinematic viscosity: above 9.5 cs	St		¹ /2 mai each for	rk : a
		4. Pour point; 21 [°] C			4 poin	nts
		5. Density: 0.83-0.9 gm/ml				
		6. API gravity:41				
		7. Specific heat: Lighter fractions ha	ave higher value			
		8. Heat of combustion: value decrea	ases from paraffin to aromatics			
		9. Viscosity index: Paraffinic base	oils have high viscosity index	and		
		naphthenic base oils have low v	iscosity index.			
		10. Paraffin has less ignition temper	rature and aromatics have high			
		ignition temperature.				
		Constituents of crude oil:				
		Crude oil is made up of the following	ng elements			
		1. carbon-84%	2. hydrogen -14%			



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	3. sulphur-1-3%	4. nitrogen, oxygen, metals,	salts- <1%	2	
	The major compounds present i	n crude oil are:			
	A. hydrocarbon				
	i) Paraffins ii) Ar	omatics			
	iii) Napthenes iv) die	enes			
	B. Non hydrocarbon				
	i) S compounds	ii)O ₂ compounds			
	iii)N ₂ compounds				
	C. Metallic compounds.				
4a iii	Fractional distillation in refin	ing process			
	Atmospheric distillation proce	ess:			
	The crude oil is preheated to 35	0-380°C in tubular furnace known a	s pipe still.		
	Hot vapours plus liquid are pass	sed through a tall fractionating colum	nn, called		
	bubble tower. It consists of a nu	umber of bubble cap trays which pro-	vide		
	intimate contact between escapi	ing vapours and down coming liquid	. Heavier		
	hydrocarbons condense more qu	uickly and settle in lower trays and li	ghter		
	hydrocarbons remain as vapour	for a long time and condense on hig	her trays.	2	
	Light gases like methane, ethan	e etc pass out from the top of the col	umn,		
	petrol are formed in the top tray	vs, kerosene and gas oils in the midd	le and fuel		
	oils at the bottom. Residue draw	vn from the bottom is send to a vacu	um		
	distillation unit or burned as a fu	uel or used as a feed stock for cracki	ng units.		



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	F= ·	-> Gases (C1-(4)		
		3		
		→ Petroleum ether ((s-Cr)		
		-> Graeoline (C5-Cg)		
	•	→ Naphtha (Cq-C10)		
		\rightarrow kerosene $(C_{1b}-C_{1b})$		
		-> Dieseloil (C10-C15)		
		ish had		
Oil Fuenace at 400°C		Heavy oil (Heavy distillate) (Residue)		
Vacuum Distillation •	·	<u></u>		2
The residue from the atmospheric	c distillation	column is send to vacu	ım	
distillation unit where absolute pr	ressure is m	aintained at 10 to 40mm	of Hg	
using multiple stages of steam jet	t eiectors. V	acuum tower may produ	ce gas	
oils lubricating-oil base stocks a	and heavy re	esidues	0	





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	Avench Residue H/E from Furnace atm-dibillation Soaker So	2
4 b	Attempt any ONE of the following	06
4b i	Delayed coking: Initially the heavy feedstock (residue from atmospheric distillation unit) is f to a furnace which heats it to high temperature (480-510°c) at low pressur (25-30 psi) and is designed & controlled to prevent premature coking in t heater tubes. The hot mixture is passed from the heater to one or more cok drums where it is held for approximately 24 hours until it cracks into light products. Vapours from the drums are returned to fractionators, where ga naphtha etc are separated out. After the coke reaches predetermined level one drum, the flow is diverted to another drum to maintain continuo operation. Full drum is steam stripped to remove uncracked hydrocarbor cooled by water injection and decoked by mechanical or hydraulic methods.	ed es 3 he er er as, in us as,

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		Flowsheet Resude Ether Reactor 200-300 atm Co +H2 Cynthesci 3 3 4 4 1 1 1 1 1 1 1 1 1 1 1 1 1	3
5		Attempt any FOUR of the following	16
5	a	Strength of Indian Petrochemical industry are	
		1. Lechnically sound man power.	
		2. All types of transportations are available.	1/2 mark
		4 Atmospheric conditions are good	each for any
		5 Consolidation of the Indian Petrochemical industry in the last few years	4 nointe
		6 Most of the petrochemical players have integrated facilities, thereby	+ points
		o. most of the performant phayers have integrated racinties, thereby	

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		reducing external dependence to a large extent. Further, petrochemicals	1		
		business being a high value add, would add further to the profitability of	f these		
		integrated companies.			
		Weakness of Indian Petrochemical industry are			
		1. Crude oil production is less.			
		2. Depending on Middle East countries			
		3. Incompetency of rupees with dollar.			
		4. Low bargaining power vis-a-vis the suppliers: Input costs form near	ly 50%		
		to 60% of the raw material costs.		¹∕₂ marl	ς.
		5. Low Bargaining power vis-a-vis customers: In case of increase in in	nput	each for a	any
		costs, the companies might not be able to pass on the rise to the consume	ers as	4 point	s
		the prices of products is highly influenced by factors such as internation	al		
		prices and supply.			
5	b	Vacuum distillation:			
		Heavier fractions from atmospheric distillation unit that cannot be d	listilled		
		without cracking under its pressure & temperature conditions are v	vacuum	4	
		distilled. Vacuum distillation is simply distillation of petroleum fract	tions at		
		very low pressure to increase volatilization & separation. In most	system		
		vacuum inside the fractionators is maintained with steam ejector & v	vacuum		
		pumps, barometric condensers or surface condensers. The inject	tion of		
		superheated steam at the base of vacuum fractionators further reduc	ces the		
		partial pressure of hydrocarbons in the tower, facilitating vaporiza	tion &		
		separation.			

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	To vacuum system	
	Vacuum gas oil	
	Residue trom atmospheric distillation Unit	
_	a for the second of and a second of the second of the	
	Explanation: Isomerization is used to convert normal paraffins to isoparaffins Catalyst: Aluminiumtrichloride, HCl is the promoter. Temperature: $100-150^{\circ}$ C. Pressure: $17-27$ atms C-C-C-C - C - C - C - C - C - C - C - C	2
	Feed stock (n-paraffins) is dried, preheated and fed to a reactor where efficient contact between reactants and catalysts takes place. HCl and make up AlCl ₃ are also added. AlCl ₃ recovery by condensation or distillation is necessary because it is volatile in reactor conditions and slightly soluble in	2 2 5 1

 $C_4H_8 + i C_4H_{10} \rightarrow 2,2,4$ trimethyl pentane

Alkylation, in petroleum refining is a chemical process in which light, gaseous hydrocarbons are combined to produce high-octane components of gasoline. The light hydrocarbons consist of olefins such as propylene and butylene and isoparaffins such as isobutane. These compounds are fed into a reactor, where, under the influence of a sulfuric-acid or hydrofluoric-acid catalyst, they combine to form a mixture of heavier hydrocarbons. The liquid fraction of this mixture, known as alkylate, consists mainly of isooctane, a compound that

2

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	$\begin{array}{rcl} i & & \hline C_4 H_{10} + & C_3 H_6 \longrightarrow i \longrightarrow C_7 H_{16} \\ i & & \hline C_4 H_{10} + & C_4 H_8 \longrightarrow i \longrightarrow C_8 H_{18} \\ C_3 H_6 & + & C_6 H_6 \longrightarrow \text{Isopropyl benzene} \\ C_2 H_4 & + & C_6 H_6 \longrightarrow \text{Ethyl benzene} \end{array} \right]^{\text{Petrochemicals}}$	
5 e	Definitions:	
	Cetane number:	
	It is defined as the percentage volume of n-cetane in a mixture of n-cetane and	2
	heptamethylnonane that gives the same ignition delay as the fuel under	
	consideration.	
	Ignition temperature:	
	The lowest temperature at which a material can catch fire and burn	2
	continuously without the aid of external firing agencies.	
6	Attempt any TWO of the following	16
6 a	Manufacture of butadiene:	
	Reaction:	
	Main reaction- $C_4H_{10} \rightarrow CH_2 = CH.CH = CH_2 + 2H_2$	2
	Side reaction- $C_4H_{10} \rightarrow C_4H_8 + H_2$	
	Explanation:	
	A refinery gas of C4/C5 containing n-butane with some isopentane is mixed	
	with recycle gas & preheated to reaction temperature .prior to contact with	
	catalyst in a fixed bed, regenerative heating reactor system. The temperature of	
	reaction at start of make period is 650°C, dropping to 550°C at the end before	
	switching to regeneration. The pressure is low 120-150mm absolute, to force	2
	reaction to right. The product gases are oil quenched, compressed, cooled&	
	separated from the light ends by absorption in naphtha followed by stripping.	

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c	Propylene oxide:	
	Reaction : It is produced via chlorohydrin route.	
	1. Chlorhydrination : $CH_3CH = CH_2 + HOC1 \rightarrow CH_3 - CHCl - CH_2OH$	
	2. Dehydrochlorination:	2
	$2CH_3- CHCl- CH_2OH + Ca(OH)_2 \rightarrow CH_3 CH CH_2O + CaCl_2 + 2H_2O$	
	Description:	
	Propylene, chlorine & water are introduced into the bottom of a packed tower	
	where chlorohydrin is formed. The reaction mechanism is formation of	
	hypochlorous acid which reacts rapidly with propylene. Reaction is exothermic	2
	and maximum tower temperature is held at 50° C by admitting cold water.	
	Unreacted propylene is scrubbed with NaOH to remove HCl. The liquid	
	stream containing chlorohydrin is drawn and neutralized with lime. Then it is	
	steam stripped to remove propylene oxide in to the overhead condenser. The	
	condensate is a mixture of oxide, water and small amount of propylene	
	dichloride and other organics. Then it is fractionated to separate propylene	
	oxide.	
	Flowsheet	

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