Thermal Cracking of Hydrocarbons: Evaluation of Various Feedstocks

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Project

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By
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Guided By
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Abstract

Thermal cracking of naphtha, gas-oil, light hydrocarbons such as Ethane, Propane, Butane and their mixtures is an important process for production of Ethylene, Propylene, Butadiene and Aromatics which are basic feedstocks of petrochemical industries. Experiments were carried out in bench scale cracker which allows cracking of different hydrocarbon feedstocks. The report presents evaluation of various feed stocks experimentally and also by SPYRO model simulation. Several runs were carried out in bench-scale cracker unit with different operating conditions that would simulate commercial plant performance with respect to yields. The optimum run conditions for Ethane cracking are: Coil Outlet Temperature (COT) : 810°C; Water to Hydrocarbon ratio : 1; Residence time: 0.25s. The optimized process conditions for Naphtha feed are; COT: 810°C, Ratio: 0.35, Residence time: 0.5 sec. In case of mixed hydrocarbon feed DMDS (Di methyl disulfide) addition was found effective than addition of DEDS (Di ethyl disulfide) as coke formation was reduced by addition of DMDS. For Cyclohexane cracking the yield of 1-3 Butadiene was more compared to other feeds. For Also effect of run length on coke formation was studied using naphtha as feed. Initial coking rate is very high which gradually decreases and then becomes constant. Simulations of different hydrocarbon feed were carried out in SPYRO model to study yield patterns of olefins.

Keywords: Thermal Cracking, Coke, Naphtha, SPYRO.

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Nomenclature

Pr	Prandtl Number
Re	Reynolds Number
R	Gas constant
t	Time, s
T	Temperature, ℃
P	Pressure, psi
L	Length, cm
ρ	Density, g/cm^3
µ	Viscosity of fluid, Pa*s
v	velocity of fluid, cm/s
A	Area, cm^2
V	Volume, cm^3
Vr	Volume of thermo well, cm^3
Vt	Effective Volume for the Reaction, cm^3
di	Inner diameter of tube, cm
E	Activation energy
f	fluid friction factor
C	Molar concentration of component, mol/cm^3
COT	Coil outlet Temperature, ℃
DMDS	Di methyl disulfide
DEDS	Di ethyl disulfide

Chapter 1

Introduction

1.1 Ethylene & Propylene Demand and Supply

Ethylene is a basic building block in the petrochemical industry due to its use as main raw material for intermediate base chemicals, such as Polyethylene, Ethylene oxide, and Styrene. These chemicals are useful in numerous consumer products. Around 60% of the total Ethylene demand is needed for the production of polyethylene. The major usage of polyethylene is in plastic films for packing and all kinds of bags. Ethylene oxide is a raw material in the production of polyesters, ethylene glycols, surfactants and detergents.[1]

The production of Ethylene has been ruled by the thermal cracking process with a global production of ~146 million tonnes per year by 2014. Propylene is a main adjacent product with capacity of ~58 million tonnes per year. Worldwide ethylene production will increase from 146 million tons per year in 2014 to 200 million tons per year by 200, an rise of 54 million tons per year. Of this progress, 24 million tons of production will be Ethane and LPG based, and 15 million tons will be Naphtha-oriented production.[2] Continuous investigation and efforts are made to attain enhanced ethylene yield and lesser energy consumption. Also, the usage of unconventional feed stocks such as biomass, natural gas, synthetic feed stocks from Fischer-Tropsch, methyl alcohol, and ethyl alcohol has also been chased.

1.2 General Overview of Thermal Cracking

Thermal cracking of hydrocarbons is an endothermic process. Thermal cracking is performed in tubular reactors made of heat resistant Fe-Ni-Cr alloys at extreme situations of high temperatures in the range of 800-950℃. The hydrocarbon feed is diluted with steam and heated in a furnace. In recent cracking furnaces, the residence time is reduced to milliseconds to increase yield, resultant in gas velocities quicker than the speed of sound.

The gases exiting the reactor are speedily quenched in a transfer line exchanger (TLE) [3]. This is done so as to prevent the loss of valuable products through secondary reactions.

The products from steam cracking obtained are highly affected by feed composition, Reactionj temperature, residence time, Hydrocarbon to steam ratio. Lighter the hydrocarbon such as ethane, propane, LPGs yields more ethylene, propylene, and butadiene. Heavier hydrocarbon feed cracking products comprise benzene, toluene, xylene fractions and other aromatics.

An inherent problem of the cracking is the formation of coke and deposition as a layer on the internal surface of the tubular reactors and the TLEs. The buildup of coke during the commercial steam cracking of hydrocarbons affects in order that it decreases heat transfer, a decrease of the tube cross section, and an increase in pressure drop. Due to coke build-up and unavailability of the furnace for cracking also affects in economic point of view. It reduces the profitability. Likewise, material destruction and also coil damage can occur. Coke build-up in the TLE rises the temperature of the leaving gases thus hindering selectivity.[4]

1.3 Thermal Cracking Mechanism

During Thermal cracking number of reactions takes place; most of the reactions proceed through free radical mechanism. Below Ethane cracking mechanism is explained and the key reactions that occur are [5]:

Initiation

In initiation step single molecule breakdown into two free radicals. Only a minor part of the feed molecules truly undergo initiation, but these reactions are essential to yield the free radicals that would carry out the remaining reactions. In steam cracking, initiation generally includes breaking a chemical bond among two carbon atoms, rather than the bond amongst a carbon and a hydrogen atom.

$CH_3CH_3 \rightarrow 2\ CH_3$

Hydrogen Abstraction

Hydrogen abstraction is step in which a free radical eliminates a hydrogen atom from another molecule, and transforming the second molecule into a free radical.

$CH_3\bullet + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2\bullet$

Radical Decomposition

In radical decomposition step, a free radical breakdown into two molecules, one an alkene and another free radical. This is the process that gives alkene products.

$CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + H\bullet$

Radical Addition

Radical addition step, is opposite of radical decomposition reactions, a radical reacts with an alkene to form an only, bigger free radical. Aromatic products are obtained from these processes.

$CH_3CH_2\bullet + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2\bullet$

Termination

This is final step in which two different free radicals reacts with each other to give products. No free radicals are produced in termination step

$CH_3\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_3$

$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + CH_3CH_3$

1.4 Coke formation in Thermal Cracking

The coke buildup on the inner walls of reactor decreasing the overall heat transfer coefficient and increasing the pressure drop across the reactor. This leads to decrease in run length of both the pressure drop across coil and coil temperature with ultimately leading to shut down of plant. The coke buildup inside the tube will be governed by (i) Type of Hydrocarbon feedstock and the coking forerunner (ii) hydrocarbon partial pressure (iii) thermal situation of coil (iv) mass velocity. Governing coking rate leads increasing the severity of the furnace to raise conversion rate, decreasing the cycle rate and unloading downstream preventing equipment which rises output.

Regular decoking action effects in loss of production which further has effect on the coil lifetime and rise fuel and utility expenses. Run length amongst two consecutive decoking differs depending upon the installation and the nature of feed stock, but can be founded at some weeks normally. In steady conditions, a furnace running on naphtha can run for 60 days without decoking. Nevertheless, run length is all the time smaller because of the unavoidable fouling of the quench boiler. In general, run length of 90 days for ethane feed, 65 days naphtha and 40 for gas oil.

Scope and Objectives of Project

1. Evaluation of various feedstocks both experimentally and theoretically.
2. Experiments would be carried out in a bench scale cracker.
3. Optimization of process parameters for maximizing yields of desired products.
4. Study the effect of run time on coking with Naphtha as feed.
5. SPYRO Model learning and simulations.
6. Prediction of yields using SPYRO model to evaluate different feeds before experimentation in bench scale cracker

Chapter 2

Literature Review

2.1 Commercial Cracking Yields

2.1.1 Cracking Conditions

Maximum Industrial cracking is to yield ethylene, which is performed in fired tubular reactors in which the temperature of the feed rises regularly from the starting to the output. Usually reactor inlet temperatures are 400–600℃ and is known as cross over temperature. Also coil outlet temperature (COT) is 800–850℃ subject to type of Hydrocarbon feed to be cracked. Cracking temperature differ depending upon feedstock. Table 2.1 shows Steam to Hydrocarbon ratios used at a coil outlet for different feedstocks at pressure of 23.93 psi to 32.634 psi.

Maximum Ethylene production requires

- Lighter Hydrocarbon feed.
- Coil outlet temperature must be high.
- Less partial pressure of Hydrocarbon.
- Shorter residence time in the radiant coil.
- Sudden cooling (Quick quench) of the cracked gases.

These conditions maximize the yield of olefins and minimize high molecular mass aromatic components. Material balance and conversion are calculated by matching the hydrogen, sulfur content, carbon of the feedstock with that of the cracked gas. This kind of analysis process is generally time-consuming. Only a gas-phase analysis is considered in case of faster system in which gas-liquid separation is eliminated. To reduce errors, many of samples have to be taken and analyzed as errors have many sources. To check the accuracy of the results, statistical approaches are used. [6]

Table 2.1: Standard Steam to Hydrocarbon Ratios for different feed stocks.

Ethane	0.25-0.35
Propane	0.30-0.40
Naphtha	0.40-0.50
Gas condensate	0.40-0.60
Atmospheric gas oils (cut: 180-350°C)	0.60-0.70
Bottoms of Hydrocracker (cut: 350-600°C)	0.70-0.85

2.2 Yields from Different Feedstocks

2.2.1 Ethane

Ethane cracking carried industrially in all kinds of furnaces, from small residence time to large residence time, the cracking temperatures for ethane feed at the reactor inlet is generally higher than for naphtha feed since Ethane is stable paraffin. Ethane cracking proceeds by free radical mechanism instead of simple process of dehydrogenation. The Reactor inlet temperatures are in the range of 550–600°C in case of Ethane. In commercial plants 50-70% conversion of ethane per pass, where unconverted Ethane recycled to extinction. Table 2.2 presents yields of various olefins from ethane cracking at different residence time. Shorter residence time give minor rise is yield. In case of Ethane feed shorter residence time is not much beneficial because the run- length for shorter residence time is small and therefore yield enhancement is moderate.

Table 2.2: Ethane Cracking yields at different residence time.

Conversion, Kg/Kg	65.01	64.97	65.01	65.01
Steam to Hydrocarbon Ratio, Kg/Kg	0.30	0.30	0.30	0.30
ResidenceTime, s	0.46	0.34	0.18	0.11
Yields (% wt)				
H_2	4.04	4.05	4.09	4.12
H_2S	0.01	0.01	0.01	0.01
CH_4	3.75	3.52	3.19	2.84
C_2H_2	0.44	0.47	0.54	0.75
C_2H_4	51.88	52.31	52.85	53.43
C_2H_6	34.99	35.03	34.99	34.99
C_3H_4	0.02	0.02	0.02	0.02
C_3H_6	1.22	1.13	1.06	0.97
C_3H_8	0.12	0.12	0.12	0.13
C_4H_4	0.05	0.05	0.05	0.06
C_4H_6	1.80	1.80	1.79	1.65
C_4H_8	0.19	0.19	0.18	0.16
C_4H_{10}	0.21	0.21	0.21	0.22
Benzene	0.55	0.47	0.38	0.26
Toluene	0.08	0.07	0.06	0.04

The Naphtha cracked gas containing ethane is separated, and reused to a segregated Ethane cracking furnace. This cracking is generally carried out at ethane- cracking conditions. Ethane furnace is not sufficient to crack all the Ethane capacity wise; therefore along with naphtha co-cracking is performed with ethane conversions of 40–50 %.

2.2.2 Propane

Major olefins yields from propane cracking at different residence time are listed in Table 2.3.Per pass conversion for propane is generally 90%. Shorter -residence-time furnaces for propane cracking has to be assessed cautiously, because of decrease in run length between consecutive decoking process.

Table 2.3: Propane Cracking yields at different residence time.

Steam to Hydrocarbon Ratio, Kg/Kg	0.30	0.30	0.30	0.30
Residence Time, s	0.44	0.33	0.17	0.10
Yields (% wt)				
$\mathbf{H_2}$	1.51	1.55	1.61	1.68
$\mathbf{CH_4}$	23.43	23.27	22.82	22.40
$\mathbf{C_2H_2}$	0.46	0.51	0.59	0.82
$\mathbf{C_2H_4}$	37.15	37.51	38.05	38.59
$\mathbf{C_2H_6}$	3.06	2.80	2.37	1.96
$\mathbf{C_3H_4}$	0.52	0.57	0.65	0.89
$\mathbf{C_3H_6}$	14.81	14.82	15.01	15.27
$\mathbf{C_3H_8}$	9.97	9.96	10.07	10.01
$\mathbf{C_4H_6}$	2.85	2.9	2.98	2.99
$\mathbf{C_4H_8}$	1.00	1	1.02	1.09
Benzene	2.15	2.12	2.02	1.80
Toluene	0.43	0.4	0.36	0.28
Xylenes	0.05	0.05	0.04	0.03

2.2.3 Naphtha

Naphtha in refinery obtained in the boiling range of 35–180℃, can change in boiling range, composition and dependent on source and refinery parameters. Generally naphtha cuts from 35 to 90℃ (light naphtha), 90–180 ℃(heavy naphtha) and 35–180 ℃ (full range naphtha) are cracked. Currently Naphtha is the major raw material for ethylene cracking, with full range naphtha's being cracked maximum. Olefinic yields from naphtha cracking at medium severity is presented in Table 2.4.

Table 2.4: Yields from medium-severity Naphtha Cracking.

Steam to Hydrocarbon Ratio, Kg/Kg	0.45	0.45	0.45	0.45
ResidenceTime, s	0.48	0.35	0.18	0.11
Yields (% wt)				
H_2	0.90	0.92	0.94	0.96
CO	0.04	0.04	0.03	0.04
CO_2	0.00	0.00	0.00	0.00
H_2S	0.00	0.00	0.00	0.00
CH_4	15.23	14.91	14.31	13.82
C_2H_2	0.44	0.47	0.53	0.71
C_2H_4	27.95	28.45	29.24	29.87
C_2H_6	4.59	4.23	3.57	3.14
C_3H_4	0.71	0.76	0.87	1.21
C_3H_6	15.38	15.64	16.09	16.43
C_3H_8	0.53	0.51	0.48	0.47
C_4H_4	0.12	0.13	0.16	0.20
C_4H_6	4.54	4.79	5.28	5.79
C_4H_8	4.41	4.52	4.75	4.95
C_4H_{10}	0.42	0.44	0.47	0.49
Benzene	7.45	7.12	6.5	5.85
Toluene	3.26	3.10	2.82	2.46
Xylenes	1.18	1.16	1.12	0.97
Ethylbenzene	0.62	0.62	0.64	0.63
Styrene	1.21	1.14	1.00	0.88
Pyrolysis gaoline	7.70	7.96	8.52	8.79
Pyrolysis fuel oil	3.32	3.09	2.68	2.34

Lesser the residence time more the olefin yields. From High- severity cracking most advantage of a selective cracking coil is attained. In this almost 5%feedstock saving can be achieved by shorter residence- times. Therefore very careful research is needed similar to gas cracking. Combination of Long run length and short residence time gives maximum yearly furnace throughput.

2.3 Factors Affecting Yields of Olefins Production by Thermal Cracking

Several process conditions (e.g. the cracking temperature, dilution, etc.) can either have a positive or a negative effect on the desired product spectrum. In the next paragraphs the effect of the selected feedstock, the set value of the dilution, the cracking temperature and the residence time is discussed.[7]

Feedstock

Various feedstocks produce different ethylene yields and ranges of products. Generally, as the feedstock gets heavier, the yield of ethylene reduces and other products such as propylene, butadiene and benzene become more significant. Heavier petroleum fractions such as gas oil or vacuum gas oil (VGO) are also subject to an increased coke deposition resulting in a more frequent shutdown of the steam cracker.

Cracking Temperature

Since cracking reactions are endothermic, maximum olefin production is realized at high temperatures. Higher cracking rate is achieved with higher cracking temperatures. Also this allows lower partial pressures or shorter residence times. At 500 ºC hydrocarbon chain tends to crack in the middle creating high molecular weight olefins, while higher temperatures leads chains to crack at the ends and form lower olefins.

Residence Time

Short residence times (a very less hundred milliseconds) increase the light olefin selectivity whereas long residence times allow secondary reactions to form oligomers and coke. Note that the effect of the residence time is strongly related to the effect of the temperature profile.

Dilution Ratio

The cracking reactions increase the number of moles. Hence, from the thermodynamic point of view, cracking of hydrocarbons into olefins and hydrogen is favored at low pressure. To reduce the hydrocarbon partial pressure generally steam is introduced. The amount of steam used is normally expressed as the mass ratio of steam to hydrocarbon and depends on the type of hydrocarbons fed. For the cracking of ethane, the steam dilution usually amounts between 0.2 and 0.4 kg steam/kg ethane. For the cracking of higher hydrocarbons, the dilution is located between 0.4 - 0.6 kg steam/kg hydrocarbon in general. Standardized procedure is required to determine the complete yield patterns

for a commercial cracking process, particularly if the Hydrocarbon is changed from ethane to naphtha and gas oil. The effluent from furnace is rapidly quenched and separated into gaseous and liquid fractions. Then both gas and liquid products are analyzed separately and then merged to obtain complete cracked gas analysis.

2.4 Classification of Coke

Due to Catalytic action of metal components as those acts as active sites, Catalytic coke is formed. [8](Figure 2.1)

– Metal components, typically Nickel and Iron, catalyse hydrocarbons to remove Hydrogen.

– Coke formed due to this catalytic action is very hard so, called hard coke and tough to remove.

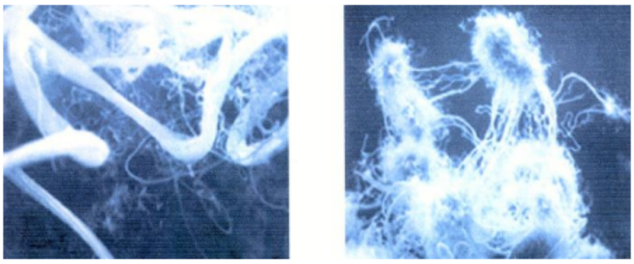

Figure 2.1: Catalytic Coke.

Pyrolytic coke mainly divided into condensation coke and gaseous, is quite soft and easy to eliminate than catalytic coke. (Figure 2.2)

– Condensation coke is formed by condensation, dehydrogenation and polymerization of heavy aromatic compounds.

– Gaseous coke is obtained by dehydrogenation of such light olefinic hydrocarbon as acetylene.

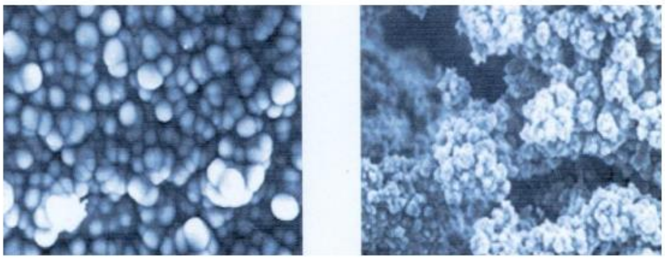

Figure 2.2: Pyrolytic Coke.

2.5 Coking in Transfer Line Exchangers

- Gas from the cracking furnace carrying coke precursors is rapidly quenched to avoid the secondary reaction in the TLE.

- Coke formation is common at the inlet cone wall, internal of the TLE tubing and on the tube sheet surface.

- This coking reasons two difficulty, i.e. a higher pressure drop and spalling either of which can lead to decrease product and operational outages for decoking. [8]

2.6 Steps Leading to Coke growth during Thermal Cracking of Hydrocarbons

Thermal cracking of hydrocarbons is the eaisest and oldest technique for petroleum refinery processes and is considered as the key process for the production of light olefins such as ethylene. The thermal cracking of hydrocarbons mainly proceeds through a free radical chain mechanism. Through abstraction and addition reactions radicals are mostly obtained. The desired gas-phase olefins are formed from decomposition of radicals by β-scission. In opinion of the major of elementary steps considered such a model is of general applicability. Usage of theoretical calculations to provide kinetic and thermodynamic data is allowed due to fundamental nature of the elementary steps to get microscopic insight in the elementary reaction steps of the coke formation system. Development of an accurate and broadly applicable model is major one of the challenge for assigning of values for rate coefficients of the separate reactions occurring in the reaction system. The basic reaction steps that lead to incorporation of carbon atoms and growth of the coke surface can be divided in five classes of reversible reactions (Figure 2.3)

During cracking process, highly unwanted carbon-rich products are formed on the internal surfaces of the reactor leading to the formation of a coke layer. This coke deposit has a undesirable effect on the effectiveness of the cracking unit. Initially coke is formed by a heterogeneous catalytic mechanism in which the properties of the internal tube surface play an vital role. Heterogeneous non-catalytic mechanism becomes important as the metal surface is covered with coke the catalytic activity of the metal particles reduces. [9]

(i) Hydrogen abstraction reactions by gas phase radicals and reverse reactions.

(ii) Substitution reactions by radicals at the coke surface and reverse reactions.

(iii) Addition reactions of radical surface species to gas phase olefins and the inverse ß-scission of a radical surface species in smaller surface species and gas phase olefins.

(iv) Addition reactions of gas phase radicals to olefinic bonds in a surface species and the inverse decomposition of radical surface species to gas phase radicals and olefinic surface species.

(v) Cyclization of radical surface species and decyclization.

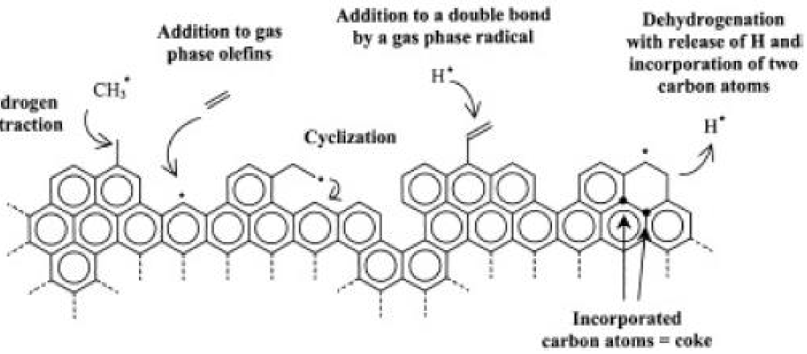

Figure 2.3: Reaction Steps Leading to Coke Growth.

2.7 Technical Approaches for Reduction of Coke Formation

2.7.1 Additives

Additives are generally mixed in a very small proportion (0.01-0.1g) with the water to mitigate coke formation. If the additive is an inhibitor then coke formation is minimized. If the additive is a catalyst, then the reactions between coke and steam are catalyzed or promoted. In such case the concentration of CO, CO2 and H2 is increased.

Chemical additives used for coke reduction include sulphur based, phosphourus based and aqueous salts of IA and IIA metal as well as proprietary silicon and phosphorus-based compounds. Each works on the same principle of forming a diffusion obstacle. By forming this obstacle, catalytic coke is reduced. The main benefit of phosphorus oriented chemicals is their thermal stability but they are kinetically slower than the sulfur compounds. These methods are not extensively used, as they are comparatively costly. Nevertheless, the gasification reaction was found to have less impact on the length of catalytic coke. The gasification reaction catalysed by potassium acetate eliminates the noncatalytic coke nearby the filamentous coke. [10]

2.7.1.1 Sulphur Based Additives

Sulfur based additives e.g. mercaptans, dimethyl sulfide and dimethyl disulfides have been conventionally treated into the cracking coil after a fresh decoking cycle. These sulfur compounds convert the metal oxide sites on the tube wall surfaces into metal sulfides. Though the main goal is to decrease carburization, it also decreases catalytic coking.

Effect of Dimethyl Disulfide (DMDS) on Coke Formation during thermal Cracking of Hydrocarbons

The effect of various dimethyl disulfide (DMDS) addition procedures i.e. continuous addition, presulfidation and presulfidation followed by continuous addition, on CO production and on coke deposition in the reactor and in the TLE during naphtha cracking is studied. Presulfidation decreases CO production. However, to obtain a low and stable CO production, sulphur is added constantly. The effect of sulfur addition on coke formation in the reactor can strongly differ from its influence on coke formation in the TLE. In the reactor, as well as in the TLE, the observed effect of sulfur addition is complicated and powerfully depends on the method Used. The optimum operating conditions for reducing CO production and reducing coke formation consist of presulfidation followed by continuous adding. Sulfur has limitations, as the metal sulfide layer inclines to get demolish by flaking or even liquefied in the case of nickel sulfide. SEM analysis of the coke samples obtained from the thermal cracking of n-hexane indicated that application of DMDS leads to a significant change in the coke morphology. EDX investigation specified that use of DMDS causes a substantially alteration in the metal content and distribution in both the alloy surface and the coke layers. The effect of the addition of CS_2, CS2, DMS, DMDS and Disulfideoil in Naphtha feed was found that for a given concentration of sulphur in the feed, the coking rate decreases in the order.

Dimethyl disulphide > Disulfideoil > Dimethyl sulphide > Carbon disulphide. [11, 12]

The sulfur based components that can be used include dimethyl disulphide, hexamethyl disiloxane, thiophene, benzopthiphene,dibenzyl sulphide,dibenzyl disulfide,organosulphur compounds,carbon disulphide and thichemicals. Literature on sulfur based additives are presented in Table 2.5.

Table 2.5: Sulphur Based Additives

Patent No.	Recipe	Effect on coke reduction
US 7,604,730B1 Phillips Petroleum Company	Mixture of dimethyl disulphide and hexamethyl disiloxane having a Si: S atomic ratio of 2:1.	66 % reduction in coke formation.
US 7,604,730 B1(2009) Phillips Petroleum Company	Mixture of dimethyl disulphide and hexamethyl disiloxane having a Si:S ratio of 1:20	72 % reduction in coke formation
US 4,116,8112(1995) Philips Petroleum	Organosulphur compounds	Cycle length increased
US 6,022,472 (2000) Belgium	Mixture of hydrogen sulfide and hydrogen at 800° C for 1.5 hours and 500 ppm mercaptan water for 0.5 hour	90 % reduction in coke formation
Bajus et.al (1983)	Dibenzyl Sulfide, dibenzyl disulfide	Rate of coking decreased.
Elf atochem Co.	Thiochemicals	Reduction in CO
Reyneirs et .al(1995)	Carbon disulfide	Reduction in CO

2.7.1.2 Phosphorus Based Additives

In thermal cracking of hydrocarbons P-containing compounds are used as additives to resist coke formation and/or CO production. Statistics regarding the effect of P-containing compounds on the decomposition of hydrocarbons during thermal cracking is rare. All these compounds quicken the thermal decomposition of n-hexane. To evaluate the quickening consequence, the potential elementary radical reactions included in the thermal cracking of these P-containing compounds are suggested. Their rate coefficients are predicted depending on thermochemical data. The phosphorus based additives passivate the surface by creating phosphate layer on the coil surface.

The phosphorus based components that can be used include organo phosphorus compounds, Triethyl Phosphite(TEP), Triphenyl Phosphite(TNP), Benzyl diethyl phosphite (BDP), Triphenyl phosphite sulfide(TPPS), elemental Phosphorus, Phosphate and Phosphite mono-diesters, Phosphate and Phosphite mono-diesters, Thiophosphate esters, Triphenylphosphine, S,S,S Tri phenylhosphorotrithioates and Phosphoric triamides.Their composition is given in Table 2.6.

Table 2.6: Phosphorus Based Additives

Patent No	**Recipe**	**Effect on coke reduction**
Naberezhnova et.al (1983)	Organophosphorus compounds	Effective in controlling coke formation
Gosh & Kunzru D.(1988)	Triethyl Phosphite (TEP)	Decoking time reduced by 5-10%
Vaish S and Kunzru D.(1992)	Triphenyl Phosphite (TNP)	Decrease in coke rate
Das P. and Kunzru (1993)	Benzyl diethyl phosphite (BDP), Triphenyl phosphite sulfide(TPPS)	TPP reduces the decoking time by 4 minutes and temperature
US 3,531,394 (1970)	Phosphorus and/or Bismuth containing compound.	Coke deposition,CO formation and erosion are eliminated.
US 3,647,677 (1972)	Elemental Phosphorus	Reduction in CO
US 4,024,050 (1977) (NALCO)	Phosphate and Phosphite mono-diesters	19-30 % reduction in coke formation.
US 4,542,253 (1985) (NALCO)	Thiophosphate esters	Coke run length increased from 2-4 months
US 4,835,332 (1989) (NALCO)	Triphenylphosphine	Fouling operations are prevented.
US 5,354,450 (1994)	S,S,S Tri phenylhosphorotrithioates	82 % reduction with commercial phosphorus additive in coking rate in n-hexane cracking.
US 5,360,531 (1994)	Phosphoric triamides	Acts as coke suppressant and reduces fouling in the reactor.

2.7.1.3 Inorganic Metal Salt Additives

Potassium acetate was used as a coking inhibitor to decrease coking during naphtha cracking on a Cr25Ni35 alloy specimen that had previously been used for 8 years. Increasing mass concentration of potassium acetate the amount of coke decreases in case of cracking of 1hr. When the concentration of Potassium acetate was 400ppm 60% reduction in coke formation was observed. The effects of the concentration of potassium acetate shows that oxide scale formed on the internal surface of the cracking tube after 8 years of usage is mostly comprised of (Fe, Ni, Cr) spinel's and the needle like intermetallic compound of Cr and Fe. On the other hand, the gasification reaction was found to have less effect on the length of catalytic coke. The gasification reaction catalyzed by potassium acetate eliminates the nonanalytic coke nearby the filamentous coke, and filamentous cokes at various concentrations are carbon nanofibers with a solid structure.[13]

Alumina and silica coatings, Tin compounds, antimony compounds or both in combination with phosphorus, Chromium ,tin and antimony tin and silicon, Aluminium and antimony or aluminium, antimony and tin, Ammonium borate in water, Combination of tin, antimony and silicon, Gallium and tin, Magnesium and calcium salts, Combination of boron compounds and a dihydroxybenzene compound, Combination of boron compounds and a dihydroxybenzene compound, Group 1A+ Group 2A + Boron compound, Trimethylsilane ,Benzeneselenol ,1,1 Dimethyl,2-selenourea, Benzyl Selenide, Sulphur + Alpha-methyl-styrene and terpinolene or thiophene, Hydroquinone compound in ethylene glycol water co solvent carrier, Ammonium biborate and hydroquinone and dimethyl diselenide.Their composition is given in Table 2.7

Table 2.7: Inorganic Metal Salt Additives

Patent No.	**Recipe**	**Effect on coke reduction**
Chan K.Y.et al (1998)	H_2PtCl_6	Decreases the coking rate.
Albright L.F and Marek J.C (1982)	Alumina and silica coatings	Creates a barrier to carbon diffusion and reduces filamentous coke
US 4,551,227 (1985)	Tin compounds, antimony compounds or both in combination with phosphorus	Reduces CO selectivity by 86 %.
US 4,863,892 (1992) (Philips Petroleum)	Chromium ,tin and antimony tin and silicon	Antimony + chromium reduces CO selectivity from 19.9 to 0.28 %.
US 4,686,201(1987)	Aluminium and antimony or aluminium, antimony and tin	More than 90 % reduction in CO.
US 4,663,018(1987)	Ammonium borate in water	68 % reduction in coke formation.
US 4,692,234 (1987) (Philips)	Combination of tin, antimony and silicon	Tin+ silicon reduces CO selectivity to around 90 % in ethane cracking.
US 4,804,487 (1989) (Philips)	Gallium and tin	89% reduction in CO
US 4,889,614 (1989) (Beta labs; Forester et al)	Magnesium and calcium salts	20 % reduction with magnesium salts
US 5,093,032, 5,128,023 and 5,330,970(1994)	Combination of boron compounds and a dihydroxybenzene compound	Average 70 % reduction in coke
US 5,358,626 (1994)	Group 1A+ Group 2A + Boron compound	60 % reduction in coke
US 6,482,311 (2002)	Trimethylsilane; Benzeneselenol;1,1 Dimethyl,2-selenourea;Benzyl Selenide	Over 98% reductions in coke deposition and 93 % reduction in coke formation.
EP 2103669 (2009)	Sulphur, Alpha-methyl-styrene and terpinolene or thiophene	20 % reduction in coke formation

2.7.2 Coating Technology

Several companies have reported coils with inner surfaces that result in much reduced levels of coke formation. The following companies claim reduced coke deposits by factors of two or three: Alon Surface Technologies, Westaim Surface Engineering Products, Daido Steel, Qunataim technologies, ANK400. In all cases, thin coatings have been formed on the inner surfaces of high alloy steels. These coatings have low concentrations of nickel, iron and other metals that produce filamentous coke. At the high temperatures experienced in the coils, considerable diffusion of metal atoms occurs in the walls of the coils and metal oxides form in the inner surface. In regular non-coated coils of high alloy steels, the inner surfaces often become much enriched in oxides of chromium, manganese, aluminium, silicon and titanium [14, 15]. Simultaneously, a sub layer enriched in iron and nickel forms.

2.7.3 Coke Formation in Transfer Line Exchanger during thermal Cracking of Hydrocarbons

Oxidation pretreatment would be better compared to reductive pretreatment, since lesser amount of coke deposition in TLE. Material of construction for TLE of 15Mo3 would be better considering the amount of coke formation than the alloys made of Incoloy 800HT. The MOC of TLE plays vital role in coking rate also the pretreatment. The rate of coke deposition depends on the temperature and water-to-Hydrogen ratio and virtually independent of the concentration of mono- and diolefins and mono- and diaromatics [16]. The free radical mechanism and condensation mechanism do not contribute considerably to coke formation at the conditions used in this study.

2.8 Simulation of Thermal Cracking Process

- COILSIM1D and SimCO softwares are used to simulate the cracking process in the reactor coils. The simulation delivers complete knowledge about concentration, velocity, and temperature fields for furnaces. Comparison of the calculated product yields over me industrial numbers authenticates the simulation and shows that the change with using a predefined normalized heat flux profile is limited. [17]

- SHAHAB is a PC-based simulator developed by olefin Research Group (ORG), with simultaneous simulation of the reactor, the firebox, the convection section and transferline exchanger in steam cracking units. SHAHAB provides a detailed understanding of product, temperature and pressure distribution, coke thickness profile, reactor run length, fuel consumption and the amount of steam generated. [18]

- Complex simulations of an ethane cracking furnace, consisting reactor and furnace models with the kinetics of coke formation, states that the run length of the furnace can be increased by more than 40% by substituting the cracking tubes of circular cross section by cracking tubes of elliptical cross section. The rise of furnace heat-transfer effectiveness and the more constant circumferential heat fluxes and temperatures help the run length of the furnace with tubes of elliptical cross section. [19]
- CRACKER software provides feed classification module which can evaluate the composition of conventional components from the commercially available indices. Plant operators can know the furnace system well and easily identify the current operation and thus can make both the optimum operation policy rendering to the market and the optimum co-cracking approach according to the characteristics of the purchased naphtha by using CRACKER software. The feed evaluation module can help to find the enhanced naphtha for the plant depending on the price of the naphtha and products. [20]
- SPYRO Simulates the cracking process inside the radiant coils of steam pyrolysis furnace of Ethylene plant as well as Transferline Exchangers, Convection section, Firebox and steam system. The software allows accurate predictions of yield patterns for feed stocks ranging from gases to gas-oil at all current operating conditions.

2.9 Optimal Operation of Tubular Reactors for Naphtha Cracking by Numerical Simulation

Process gas temperature profile and steam to hydrocarbon ratio in the feed have significant influence on coking rate in tubular reactors for naphtha cracking and product yields. Ideal operation of the tubular reactor in commercial steam cracking furnace stated was first simulated in HYSYS with a molecular reaction network. The optimum process temperature profile and the optimum inlet steam to naphtha ratio were found in order to increase the process income. Different case studies then studied the impact of process gas temperature profile and inlet steam to hydrocarbon ratio so that the ethylene/propylene product yields and coking rate can be assessed. Finally, steady-state optimisation was applied to the operation of this industrial furnace.

Optimum process gas temperature is 1084.15 K at the exit of the tubular reactor. In Comparison with the standard system, COT has been raised 16.1K. The optimum COT temperature was 1084.15K. In this way, the cracking reaction is much quicker and the product yields are higher. This adds larger profit margin. Other way, due to raised temperature over the complete tube length (in the optimum temperature profile), the coking rate becomes high. Thus, the expenditure produced by tubular reactor shutdown for decoking also becomes high. The optimum steam to naphtha ratio in the feed is still 0.6. Therefore the production time between two successive decokings decreased from 41.46 days to 21 days. [21]

Chapter 3

Experimental Setup and Procedure

3.1 Experimental Setup

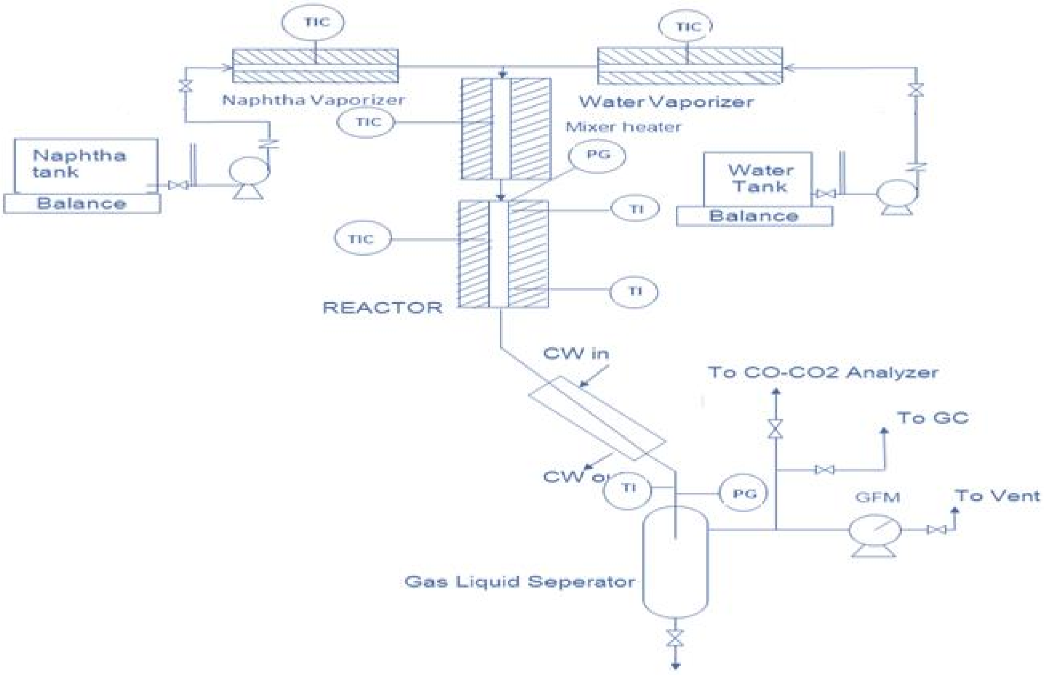

Figure 3.1: Schematic Representation of a Naphtha Cracker Pilot Plant

Naphtha and water are stored in two SS (stainless steel) tanks. The naphtha is brought from the industrial plant and it is filtered. On the other hand, water used is distilled water. The tanks are provided with two level gauges with the help of which the flow rates of the feedstock can be checked at regular intervals of time. The tanks are placed on two separate electronic weighing balances. Two metering pumps are also provided for pumping the feed to the next stage. Here cold water is circulated through the pumps for maintain the temperature. The naphtha and water are passed through their respective vaporizers (SS316) and are mixed in the mixer (also known as the convection section) before entering into the furnace (radiation section). The temperatures of the vaporizers are approximately 100°C and that of mixer is set around 500°C.The mixer outlet enters the top of the reactor tube inlet at around 540°C which is taken as the crossover temperature. Next, the reaction mixture enters the pyrolysis section (also known as radiant section) whose temperature is maintained around 830°C (COT) where the cracking occurs. The length of the reactor tube is 33 cm while its diameter is 11 mm. It is made up of Incoloy 800HT (Ni: 30-35%, Cr: 19-23 %, Fe $>$ 39.5 % by wt). The process gas temperature is measured by means of a thermocouple. The pressure gauges located at two different points- one at the mixer inlet and the other at the top outlet of gas liquid separator keeps a track of the pressure drop within the system. The furnace is 36 cm long and 26 cm wide. It is heated electronically by means of radiant coils placed inside it.Schematic representation of a naphtha cracker pilot plant is presented in figure 3.1.

The temperature of the cracked gases leaving the furnace is around 750°C. The gaseous products then pass through two transfer line exchangers (TLE's) where they are rapidly quenched to temperatures below 300° C.This is done to avoid the losses of valuable products through secondary reactions The TLE consists of two concentric tubes: the reactor effluent flows through the inner tube, while chilled water flows counter-currently through the outer tube. The chiller used is Julabo.

At the end of TLE's, there is gas liquid separator where the heavy products like Benzene, Toluene and Xylene along with condensed water are collected at the bottom and the desired gaseous products like ethylene, propylene etc. are collected at the top and analyzed. The outlet from the top of the gas liquid separator can also be connected to a gas glow meter (GFM) to measure the flow rate of the cracked gases.The cracked gases are simultaneously analyzed on gas chromatographic (GC) system. The GC used is Hewlett-Packard (HP) 6890. The yields are expressed as (%wt. of component /wt. of naphtha). The results are processed and useful data is generated for effective operation.

3.1.1 Experimental Procedure

Figure 3.2: Photograph of the Experimental Set-up

For a normal run, the furnace is turned on and the temperature is slowly increased by means of a temperature controller. The air is fed continuously inside the unit. After the desired temperature is achieved, the air flow is stopped and naphtha and water pumps are switched on. The flow rates of naphtha and water are calculated by means of the level gauges attached to the respective naphtha and water storage tanks. It is done with the help of a stopwatch i.e. for 0.2 ml of the fluid the time taken in seconds is calculated. The temperature of the furnace drops, as soon as the cracking reaction takes place inside the reactor. This reaction is highly endothermic. The bubbles formed inside the bubbler indicates that the cracking has taken place. As soon as the first bubble is seen, the bladder is connected at the top outlet of the gas liquid separator. This gas sample is then attached to a CO-CO_2 analyzer which gives the value of CO-CO_2 (vol %) in the sample. Typical material balance is carried out for an hour by noting down the weight of naphtha and water from the electronic balances, the amount of liquid product collected and the amount of gas measured during one hour period. The actual Photograph of the experimental set-up is shown in Figure3.2.

After completion of the run, the reactor is cooled. It is done by providing N_2 purge. The temperature is slowly decreased and then the unit is completely shut down. The reactor is then opened and the thermowell is weighed to measure the coke deposited on its surface. The thermowell is the then immersed in a cylinder of acetone. After it is cleaned, it is again weighed and this difference between the original weight of thermowell and the empty thermowell gives the amount of coke deposited on it known as the surface coke. The free flowing coke collected during the opening of the reactor is known as spalled coke which is also collected and measured. The coupling which is connected to the reactor is also removed and cleaned with acetone. With the help of a thin wire, the reactor tube is cleaned properly to remove any traces of coke present inside it. Next, acetone is passed through the two TLE's and kept undisturbed for an hour. The entire assembly is then made leak proof and boxed up. The reactor is then steam-air decoked.

3.1.2 Decoking

After the unit is made leak proof, the nitrogen purging is provided and the temperature of the furnace is slowly increased by means of a temperature controller. After a desired temperature is reached (i.e. 860°C) the nitrogen flow is stopped and water and air are introduced into the unit. The water pump is set to 0.920 ml/min, while the air flow is 58-60 l/hr. The decoking goes on for about 24 hours. A CO-CO_2 analysis of the gas sample is carried out every 2 hours and the readings are noted down.

3.2 Sample Preparation

Next, Four ICP (Infrared Coupled Plasma Mass Spectrometry) samples are taken for the analysis. This is done mainly to check the corrosion content. The samples are:

1. Bubbler Water. (BWR)
2. NCP (Naphtha cracking Plant) liquid layer. (LPR)
3. NCP extracted organic layer. (ORG)
4. Hot water condensate. (TLEW)

For NCP extracted organic layer the procedure is as follows:

- The NCP liquid product coming out from the gas liquid separator is collected in a container.
- This product is then transferred to a separating funnel.

1. Top layer known as the organic layer
2. Bottom layer known as the water or liquid layer.

- Now, the top layer (organic layer) is separated and 20 ml of this organic layer is collected in a beaker and 20 ml of 4 %HNO_3 is added to it.
- The solution is shaked and kept undisturbed for about half an hour.

- Again the above solution is poured in the separating funnel and the liquid layer which is formed is collected in a beaker.
- This liquid layer is filtered using Whatman's filter paper and collected in sample bottles and then sent for ICP analysis. The remaining three samples (20 ml) are collected, filtered and sent for inductively coupled plasma –mass spectroscopy (ICP) analysis.

3.3 CO-CO_2 Analysis of the Gas Sample

Figure 3.3: Photograph of a CO-CO_2 Analyzer

3.3.1 Principle of a gas analyzer

Carbon dioxide analyzers, also called CO_2 gas analyzers, are devices that can detect and quantify the amount of carbon dioxide in a sample. The most common principle used for CO_2 analyzer is the Non-Dispersive Infrared analysis (NDIR). Photograph of a CO-CO_2 analyzer is presented in Figure 3.3 and Figure 3.4 steps involved in the Injection of a gas Sample. The basic steps involved in the measurement of CO-CO_2 in a gas sample are as follows:

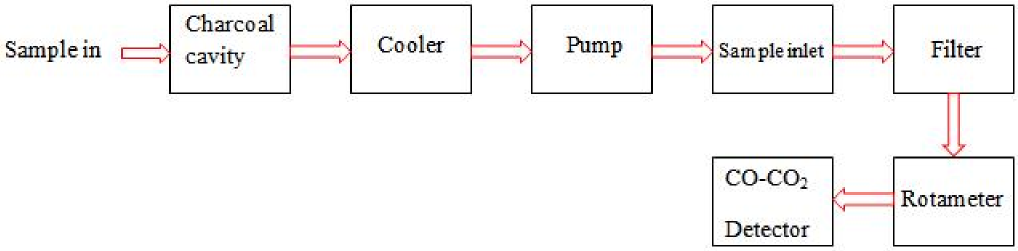

Figure 3.4: Steps Involved in the Injection of a Gas Sample

3.3.1.1 Procedure

During the cracking operation, a gaseous sample is collected in a rubber bladder at the top outlet of the gas liquid separator. The rubber bladder should be free of any gases.

- This sample is then injected into an inlet which is provided outside a CO-CO_2analyzer. Here three valves regulate the flow of gas in the analyzer so that the resulting mole percent of CO-CO_2 is obtained.
- The sample gas valve is turned on.
- N_2 purge valve is turned off .This is done to decrease the value of the readings.
- Sample/calibration valve is turned on to the sample side.
- Also the membrane pump is turned on.
- The CO-CO_2 value is shown on the screen as provided.
- The initial readings are recorded.
- Initially the value of CO-CO_2 increases to a certain extent and then decreases gradually.
- The final values of CO-CO_2 are also noted down. The difference between the final and initial values gives us the actual number in mole percent. The sample gas valve is then turned off, N_2 purge valve is turned on-to decrease the values of CO-CO_2 and the sample/calibration valve is turned on to the calibration side. The membrane pump is then switched off.

3.4 Gas Chromatography

3.4.1 Basic Principle

Gas chromatography is a method used for separation and assessing compounds that can be vaporized by decomposition. In gas chromatography, the mobile phase (or "moving phase") is a carrier gas, usually an unreactive gas such as nitrogen. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside a portion of glass or metal tubing called a column. A gas chromatograph is a chemical analysis apparatus for separating chemicals in the gas sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical compounds of a sample pass in a gas stream (carrier gas, mobile phase) at various rates dependent on their different chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. The purpose of the stationary phase in the column is to separate components, affecting each one to leaving the column at a different time (retention time). Other parameters that can be used to change the order or time of retention are the carrier gas flow rate, column length and the temperature. The gaseous compounds being analyzed interact with the walls of the column, which is coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound.

3.4.2 GC setup and Experimental Procedure for Peak Detection of Gaseous Components

3.4.2.1 GC Setup

The GC apparatus consists of two types of columns:

1. Packed column known as Pora Pack Q
2. Capillary column consisting of Plot alumina, Al_2O_3 and KCl.

The packed column is of a greater diameter as compared to the capillary column and it is connected to one of the detectors known as Thermal conductivity detector (TCD).The capillary column is connected to the Flame Ionization detector (FID). In FID, a mixture of H2: Air is charged in the ratio of 1:10.The carrier gas used is nitrogen. The oven temperature is set at 35°C and it increases at a rate of 3°C/min up to 180 ° C. The initial time set is 5 min. The analysis takes about 58 minutes In TCD, the oven temperature is set at 35°C.

3.4.2.2 Procedure for Peak Detection of Gaseous Components

1. The GC is connected to a computer where various inputs are provided. Then the system needs to be made ready for the sample to be injected in TCD or FID.

2. Initially a pure H2 gas sample is taken in a bladder and injected into the TCD by means of a syringe. The sample taken is 0.5 ml. After the first peak is obtained another sample is injected. This procedure is repeated thrice.

3. Next the sample gas i.e. the top product from the gas liquid separator is collected in a bladder and it is injected by means of a syringe in the TCD. The sample volume is 0.5 ml. This gives the hydrogen purity in the sample.

4. Now the system setting is to be changed from TCD to FID. The GC is allowed to get ready for the injection. Once it is ready, the same sample gas (0.5 ml) is injected into the FID. After some time the peaks of various components inside the gas sample is obtained.

The pure H_2 gas sample is injected in TCD. This is done 3 times. The sample gas i.e. the top product from the gas liquid separator is first injected in TCD which gives the purity of hydrogen and then the second injection is made in FID which gives the composition of constituent components in the sample gas. A graph of area vs. retention time (sec) is obtained.

Chapter 4

Results and Discussions

4.1 Ethane Cracking

Number of runs were performed with typical Ethane as feed on bench scale cracking unit. The feed flow rate and other run conditions are shown in Table 4.1. By changing the furnace set point desired coil outlet temperature (COT) was obtained.

Ethane cracking was carried out at temperature 850℃, steam dilution ratio 1 (kg of steam/kg of Ethane), and at atmospheric pressure. 1hr presulfiding was done before start of run in each run. Presulfiding step is very important step in case of gas cracking because coke formation is more in case of thermal cracking of gases and their mixtures. In presufidation 1hr 200ppm DMDS solution is feed to system at the flow rate of 44.66g/hr, COT=800℃. In all the runs presulfidation and DMDS solution was added continuously. Using Mass flow meter desired Ethane flow rate is obtained. Table 4.2 shows the detailed results of Ethane cracking.

Table 4.1: Run conditions for Ethane Cracking.

Run No.	1	2	3	4
Run time, hrs.	4	6	6	6
Ethane flow rate, g/h	44.66	44.66	44.66	44.66
Water flow rate, g/h	44.66	44.66	44.66	44.66
Ratio	1	1	1	1
Residence time, s	0.25	0.25	0.25	0.25
COT, ℃	840	850	850	850
Mixer, ℃	340	300	300	300
Presulfidation, hr	1	1	1	1

Table 4.2: Yields of Ethane Cracking.

Run No.	1	2	3	4
Run time, hrs.	4	6	6	6
Conversion, %	58	55	49	52
CO, wt.%	6.85	10.20	7.76	8.51
CO_2, wt.%	0.73	1.01	0.98	1.08
Yields (% wt)				
Methane	1.63	1.23	1.17	1.47
Ethane	41.55	45.23	51.09	47.71
Ethylene	41.83	36.18	34.04	35.09
Propane	0.00	0.00	0.00	0.00
Propylene	0.35	0.25	0.00	0.00
H_2	6.35	5.41	4.96	6.14
Gas flow meter, lit	69.74	72	60.40	70.48
Liquid weight, g	42.58	38.14	43.86	36.96
Material Balance, %	96.63	97.04	96.39	91.67

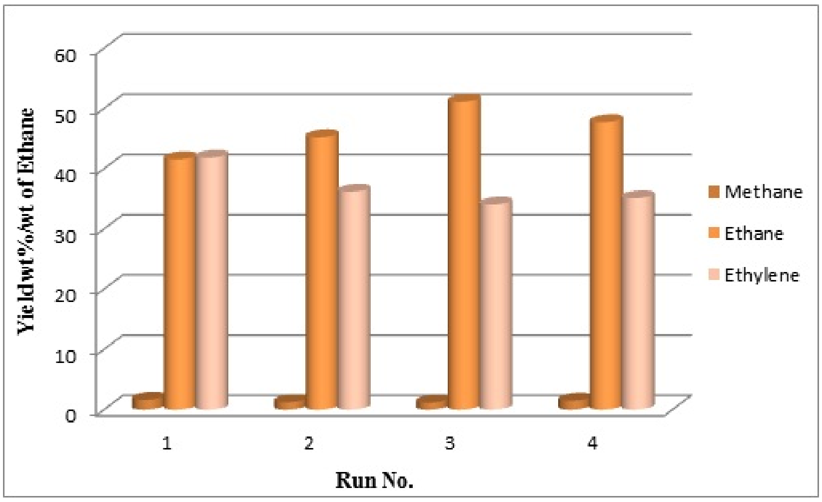

Figure 4.1: Yields of Ethane Cracking.

Initially water is feed to system before Ethane and after 1-5 mins Ethane is introduced, 50°C Temperature drop is noted in COT as soon as Ethane is feed. By increasing furnace set point stepwise desired COT was obtained. Gas product is collected in bladder as soon as product is obtained to measure initial CO-CO_2. 1 hr material balances were carried for each run. Amount of gas and liquid obtained for 1hr was measured. The conversion was around 49-58%. Practically no pyrolysis gasoline is formed during ethane cracking even less fuel oil is formed. Cracking yield pattern is presented in Figure 4.1.

As per results, maximum ethylene obtained 41.55 wt %. These same cracking conditions were repeated in order to reproduce the results but were not able to reproduce. In an average 34-36 wt % Ethylene yield was obtained. Mixer temperature and other parameters were varied in order to optimize the run conditions. In commercial Ethane cracking 50-53 % Ethylene yield is obtained. Regularly CO-CO_2 was measured during each run. Figure 4.2 shows amount CO formed during each run at different time interval.

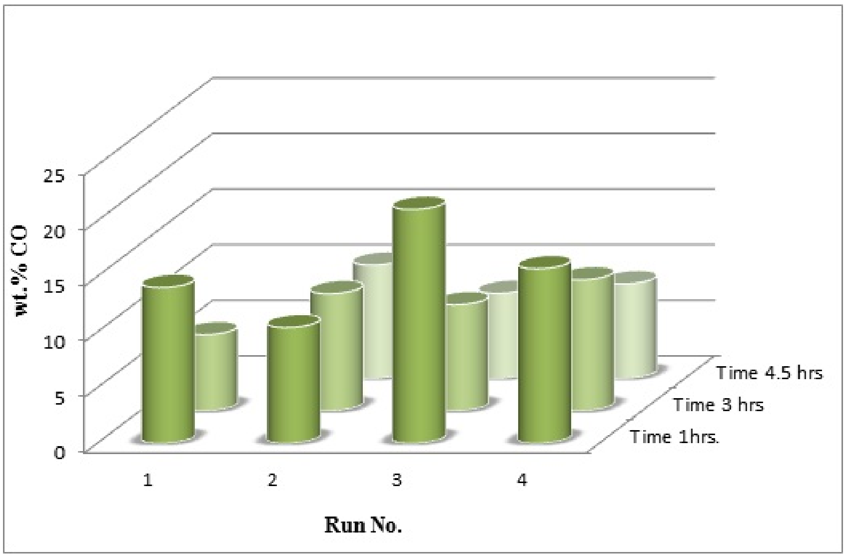

Figure 4.2: Wt. % CO formed in each Run at different time Interval.

Ni, Cr, Fe Ni, Cr, Fe and their oxides in coils promote catalytic coke formation initially. Once layer of catalytic coke is deposited, further lesser effect of coke was observed. Figure clearly shows that initially coking rate is more, as run proceeds less coke formation. Efforts have been put up in order to reduce coking rate so that it will increase the Ethylene yield and obtain better conversion.

In Ethane cracking hydrogen and Ethylene were major products while in each run methane was formed in lesser amounts. On other side Propylene, butane and propane were obtained in minor quantities. Carbon monoxide and carbon dioxide were always produced in major quantity. These results recommend that part of the ethylene firstly decomposes on the surfaces to form carbon (or coke) and Hydrogen and part of the coke deposited on the metal surfaces then reacts with to form carbon oxides and more hydrogen.

All the results got in this study indicates that at whenever Ethylene yields were lower, the joint yields of coke and carbon oxides were higher as were also the yields of Hydrogen. The bench scale cracker used in this study has large Surface to Volume ratio, also reactor diameter is small. In this unit due to high S/V ratio carbon yields were much higher as a rule than yields in industrial reactors. Scale up from this bench scale study should be done very carefully.

Steam reduces partial pressure of feed and lower the hydrocarbon partial pressure leads to increase in ethylene yields also similarly higher the reaction temperature more the ethylene yield but at the expense of coke. So optimization of operating parameters plays important role. The relative effect of steam on ethylene yields in metal reactors is opposite to that found in commercial units. The partial pressure effect for steam is main in most industrial crackers whereas the surface reactions effect was important in the small diameter reactors in this study. Steam acts to lower the partial pressure of the hydrocarbons; low partial pressure tends to promote higher ethylene yields, also ethylene yield increases with increase in reaction temperature. But steam also promotes surface reactions, such reactions lower ethylene yield.

4.2 Naphtha Cracking

Thermal cracking of Naphtha was carried out in bench scale cracker in reactor made of Incoloy 800HT. Metal content (%wt) analysis of Incoloy 800HT reactor used in the present investigation is presented in Table 4.3.

Table 4.3: Composition of Incoloy 800HT

Metal	**Incoloy 800HT**
Fe	46.8
Ni	31.28
Cr	19.47
Mn	0.89
Si	0.37
Cu	0.29
Ti	0.277
Al	0.27
C	0.073

The feed composition of Naphtha Feed used for Run No.1 to Run No 4 is shown in Table 4.4. The corresponding run conditions is also presented in same table. Objective was to optimize the base run conditions by varying ratio, Hydrocarbon flow rate, residence time, Coil outlet temperature (COT) in order to increase yield of Ethylene, propylene and other major components. Naphtha and water is pumped using metering pump and controllers are used to control temperatures. Numbers of runs were carried out. The cracking experimental setup and process explained in detail in chapter no. 3. During each run periodically gas and Liquid sample were collected and analysed. All the runs were carried out for 48hrs. System takes 1-2 hrs to stabilize. Almost 20-25 ℃ temperature drop in COT is observed as soon as Naphtha is started.

Table 4.4: Run Conditions for Naphtha Cracking.

Run No.	1	2	3	4
Naphtha Flow rate, g/h	64.19	65.069	65.065	63.33
Water Flow rate, g/h	32.09	22.77	26.027	31.66
Ratio	0.5	0.35	0.4	0.5
Residence Time, s	0.4	0.5	0.4	0.4
COT, ℃	810	810	810	810
Feed, wt%				
n-paraffins	32.84	32.84	32.84	32.84
i-paraffins	31.725	31.725	31.725	31.725
Olefins	1.81	1.81	1.81	1.81
Naphthenes	25.94	25.94	25.94	25.94
Aromatics	7.691	7.691	7.691	7.691
Reactor MOC	Incoloy 800HT	Incoloy 800HT	Incoloy 800HT	Incoloy 800HT

Table 4.5: Flow Rate and Yield data for Run No 1 Naphtha Feed

Gas, l	38	36.24	41.93	40.05	38.26
Naphtha, g	64.19	64.19	64.19	64.19	64.19
Water, g	32.09	32.09	32.09	32.09	32.09
Liquid(BTX), g	39.85	41.05	42.05	43.29	42.60
CO mole%	0.23	0.21	0.11	0.04	0.05
CO_2mole%	0.18	0.14	0.14	0.07	0.06
Yields (%wt)					
Methane	8.93	7.02	9.10	9.05	9.51
Ethane	2.30	1.97	2.36	2.26	2.32
Ethylene	22.51	19.75	24.19	23.51	24.20
Propane	0.33	0.31	0.35	0.33	0.32
Propylene	14.50	13.78	15.76	14.97	13.96
isobutane	0.17	0.18	0.22	0.23	0.17
n-butane	0.08	0.07	0.14	0.14	0.10
Propadiene	0.21	0.23	0.25	0.22	0.15
t-2-butene	0.53	0.67	0.60	0.52	0.35
1-butene	2.36	2.90	2.78	2.55	2.05
i-butene	2.43	2.78	2.74	2.52	2.15
cis-2-butene	0.40	0.52	0.45	0.40	0.28
i-pentane	0.14	0.31	0.16	0.10	0.08
1,2-butadiene	1.28	1.93	1.93	1.90	1.43
n-pentane	1.74	3.02	2.39	2.21	1.35
Methyl acetylene	0.23	0.29	0.27	0.25	0.18
1,3-butadiene	4.45	5.89	4.73	4.07	2.69
H_2	0.66	0.78	0.87	0.79	0.65
Total	63.57	62.65	69.51	66.13	62.04
Material Balance %	83.55	84.23	98.21	88.99	91.77
Surface coke, g	0.2754				
Spalled coke,g	5.0204				

During run at certain interval of time 1hr material balances were carried out in which flow rates are measured and GC analysis from which yield calculations were done. Table 4.5 shows flow rate data and yield obtained. Figure 4.3 presented shows yield pattern of major olefin components as a function of time. Figure 4.4 shows CO-CO_2data measured during run. CO-CO_2in the product stream were measured during cracking as soon as gas product started coming out from the reactor via condenser (normally after 15 min) and then once in 4 h and at the time of material balance runs. Initally CO and $CO_2$are higher due to the exposure of hydrocarbons to bare metal surface and become steady as time moves on. (BTX-Benzene Toluene Xylene)

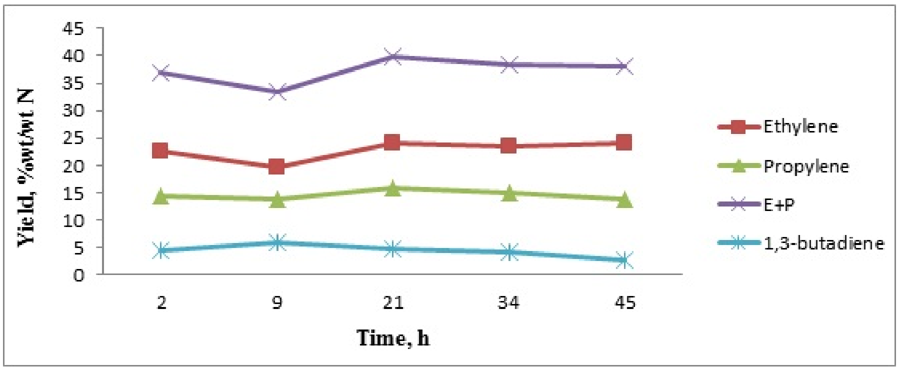

Figure 4.3: Yield pattern of major components of Run No. 1 for Naphtha feed

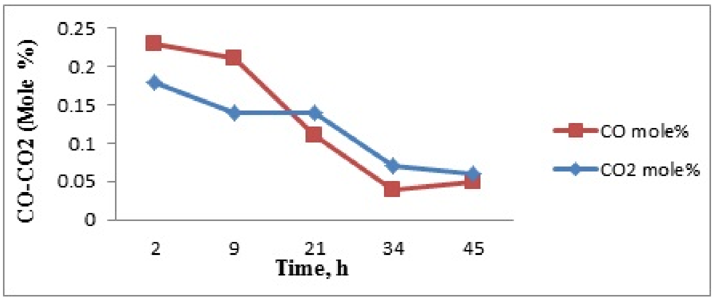

Figure 4.4: CO-CO_2 Analysis of Run No. 1.

Initially during start of run higher coke formation was observed. As Ni, Cr, Fe and their oxides in coils promote catalytic coke formation initially. Once layer of catalytic coke is deposited, further lesser effect of coke was observed.

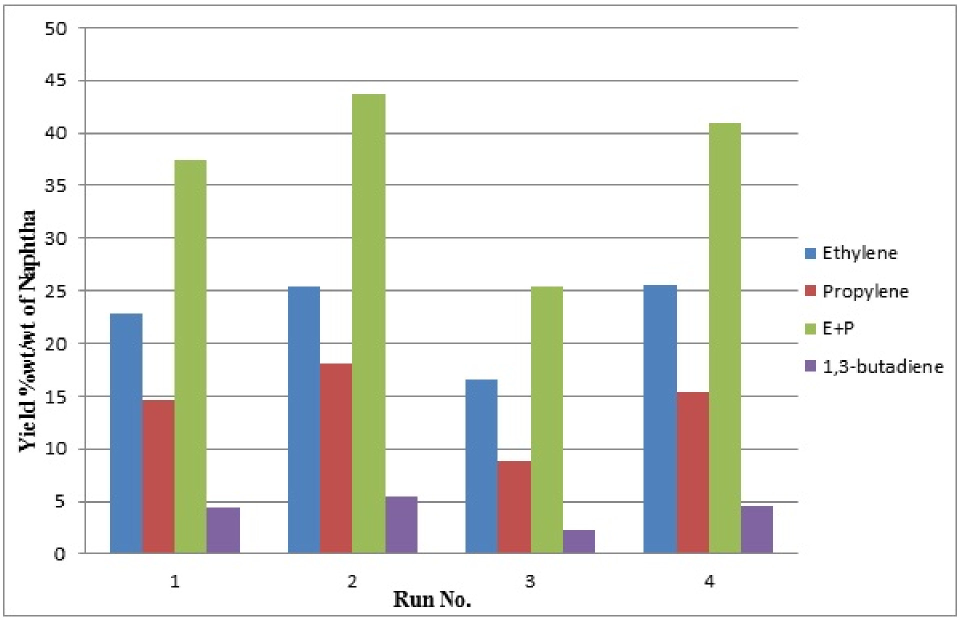

Figure 4.5: Average yields of major components obtained in Run no. 1 to 4 for Naphtha feed.

In order to optimize the run conditions, process parameters were varied. Figure 4.5 shows average yields of major components for Run no. 1 to 4. Maximum Ethylene obtained 27.14 %wt, Propylene 18.69%wt, 1-3 Butadiene 5.87%wt, at conditions COT-810℃, ratio-0.35, and residence time- 0.5s. Amount of coke formed in each run is presented in figure 4.7. Spalled coke that is free flowing coke was more in run no. 1 and surface coke was more in run no. 3.

4.2.1 Decoking of Run No.1

Table 4.6 shows Decoking Conditions for Run no.1, usually for all hydrocarbon feeds decoking is done in the range of 850- 865℃. Decoking is done in presence of air and water. Air flow rate is in the range of 50-60 litre/hr. Decoking generally done for 40-60 hrs. It depends on amount of coke formed. In every 4hrs CO-CO_2 analysed using CO-CO_2 analyser. Graph of CO-CO_2 as a function of time is given in figure 4.6.

Table 4.6: Decoking Conditions for Run No.1

Water Vaporizer	100℃
Mixer	515℃
Cross-over	475℃
Furnace Set point	713℃
COT	865℃

4.2.2 CO-CO2 Analysis of Decoking of Run No.1

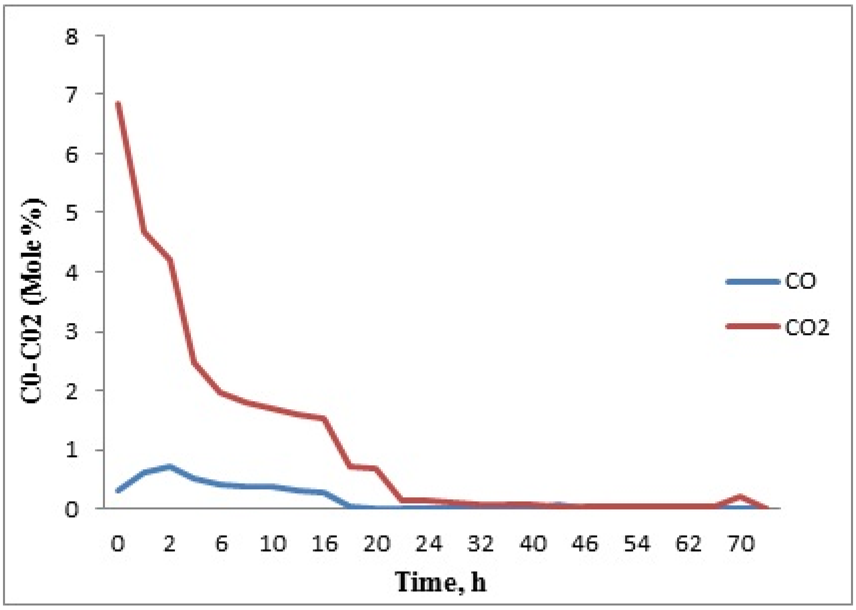

Figure 4.6: CO-CO_2 Analysis of Decoking of Run No.1.

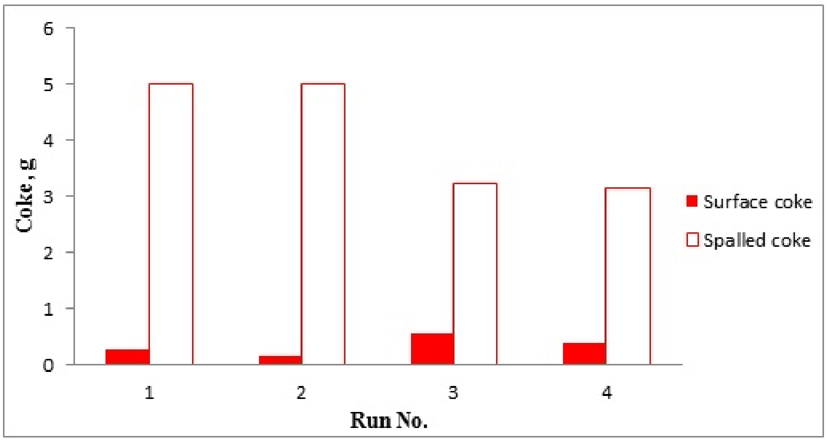

Figure 4.7: Amount of coke formed in each run in Naphtha cracking.

4.3 Mixed Hydrocarbon Cracking

Mixed hydrocarbon feed with major Straight Naphtha, Coker Naphtha and n-hexane was prepared. The feed composition is shown in Table 4.7.Two runs of each 48hrs were carried out in which, DMDS (Dimethyl Disulfide) in 1st and DEDS (Diethyl Disulfide) in 2nd as Sulfur based additives. The objective behind cracking of mixed hydrocarbon feed was to study sulphur effect on coke formation. 10kg feed was prepared, out of 10 kg feed in 5 kg of feed 1.11gm DMDS was added and 1.4392 gm of DEDS was added to remaining 5kg respectively. Run conditions for Run No. 1 and 2 are shown in Table 4.8. Both the runs were performed with the same run conditions.

Table 4.7: Feed composition of Mixed Hydrocarbon Cracking.

Mixed Hydrocarbon Feed	**wt in gms**
Iso octane	704
n-nonane	343
n-hexane	2953
Straight run Naphtha	3000
Coker Naphtha	3000
Total	10000

Table 4.8: Run conditions for feed 2 and feed 3.

	Mixed Hydrocarbon Feed 2 (5000gm) + 1.11 gm DMDS	**Mixed Hydrocarbon Feed 3 (5000gm) + 1.4392gm DEDS**
Run No.	1	2
HC Flow rate, g/h	64.19	64.19
Water Flow rate, g/h	32.09	32.09
Ratio	0.5	0.5
Residence Time, s	0.4	0.4
COT, °C	810	810

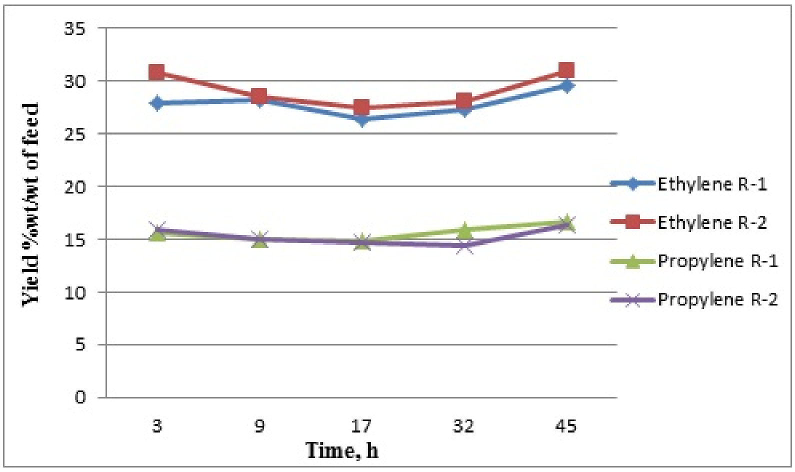

Figure 4.8: Yields in Run No. 1& 2 for mixed Hydrocarbon feed.

From results obtained it is seen that influence of DMDS was more than DEDS as the amount of surface coke and Spalled coke was lesser in addition of DMDS, as shown in Table 4.9. Also, concentration of CO in effluent gas was also lesser. The yield pattern for both runs is shown in figure 4.8.

Table 4.9: Amount of Coke formed.

Run No.	**Surface coke, g**	**Spalled coke, g**
1	0.351	2.13
2	0.373	2.456

4.4 Cyclohexane Cracking

Cyclohexane is one of the most important solvent in chemical Industries. The objective of cyclohexane cracking was to study yield of 1-3 Butadiene. 1-3 Butadiene is most important feedstock in petrochemical industries. Run conditions for cyclohexane cracking is presented in Table 4.10

Table 4.10: Run Conditions for Cyclohexane cracking.

Run No.	1
Naphtha Flow rate, g/h	52.16
Water Flow rate, g/h	26.08
Ratio	0.5
Residence Time, s	0.5
COT, °C	790

Below figure 4.9 shows a path for cyclohexane cracking. In this case it is understandable that a cyclohexyl radical must be involved in the propagation order which then leads, by β scission and ring opening, to the isomeric hex-1-ene-6-yl radical, with breakdown continuing as shown to yield ethylene, 1-3 butadiene, and a hydrogen atom that is the chain carrier. This is the comparatively good acknowledged main path for cyclohexane decomposition and appropriately accounts for the three main products. Still, the path is matter to dividing by way of stable intermediates such as but-1-ene and hex-1-ene, which result from H-abstraction reactions of the primary intermediate radicals; these steady molecules then experience further pyrolysis reactions to yield a spectrum of pyrolysis products, e.g., methane and propylene, which are seen in smaller amounts during cyclohexane pyrolysis.

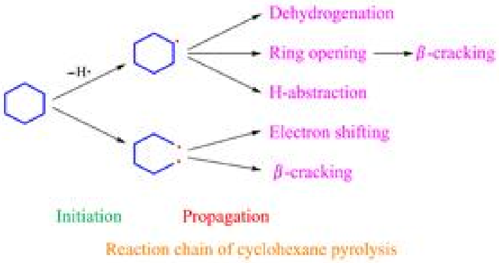

Figure 4.9: Cyclohexane Pyrolysis Pathway.

During cracking poor temperature profile was observed, also initial endotherm was around 50°C. Yield pattern of major components is shown in figure 4.10. Table 4.11 shows Yields (%wt/wt. Cyclohexane) of Run No. 1. Initially yield of 1-3 Butadiene was less and as run proceed yield increased. Surface coke =1.153 g and Spalled coke = 1.4812 g, surface coke was comparatively obtained more.

Table 4.11: Yields of Major Products in Cyclohexane Cracking (%wt/wt. Cyclohexane)

TOS	**Ethylene**	**Propylene**	**E+P**	**1-3 Butadiene**
3	20.22	4.53	24.74	7.44
14	21.59	4.50	26.09	8.47
25	20.96	4.36	25.32	8.42
39	21.29	4.42	25.71	9.64
47	20.36	4.46	20.36	11.40

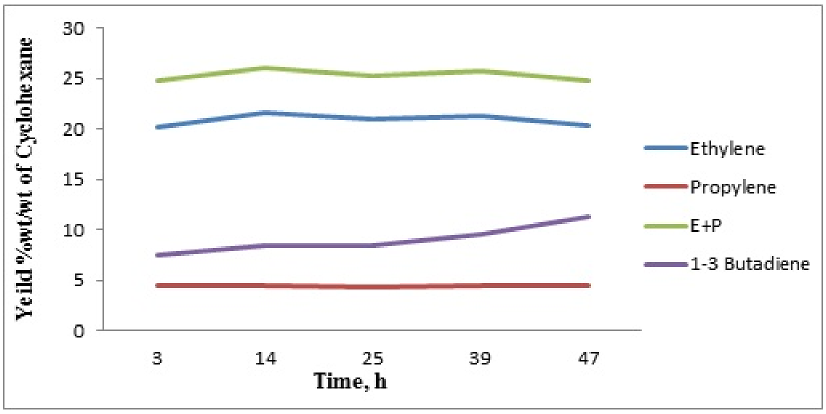

Figure 4.10: Yield pattern of major components of Cyclohexane Cracking.

4.5 Octene Cracking

Thermal cracking of octene, olefinic feed stock was also carried out. Numbers of runs were carried out to test effect of additives such as DMDS and DEDS in terms of reduction in coke formation. Table 4.12 shows feed condition and yield. Generally octene cracking is carried at lower temperature compared to other hydrocarbon cracking. Maximum Ethylene, propylene yields obtained were 26.52 wt%, 12.04 wt% and 1-3 Butadiene yield 7.35 wt % as shown in figure 4.11. Better temperature control was observed throughout the run. Addition of DMDS was found to be more effective compared to DEDS, because amount of coke formation was less.

Table 4.12: Run condition and yields for Octene cracking.

Run No.	**1**	**DMDS**	**2**	**DEDS**
Octene flow rate, g/h	73.21		73.21	
Water flow rate, g/h	36.61		36.6	
Steam dilution ratio	0.50		0.50	
Residence time, s	0.4		0.4	
COT, ℃	750		750	
Yield (%wt)	MB1	MB2	MB1	MB2
TOS, hrs	3	15	3	15
CO	4.599	2.411	4.368	4.065
CO2	1.275	0.914	0.316	0.297
Methane	5.03	5.08	6.73	6.40
Ethane	3.09	3.08	3.51	3.52
Ethylene	22.92	23.89	26.68	26.52
Propane	0.49	0.50	0.59	0.59
Propylene	11.67	12.04	10.97	10.92
isobutane	0.01	0.01	0.01	0.01
n-Butane	0.04	0.08	0.16	0.15
Propadiene	0.17	0.18	0.19	0.19
t-2butene	0.05	0.06	0.09	0.09
1-butene	0.46	0.41	0.64	0.01
i-butene	4.50	4.85	4.10	0.63
cis-2-butene	0.43	0.46	0.57	4.13
i-pentane	0.37	0.35	0.49	0.59
1,2butadiene	0.02	0.02	0.05	0.49
n-pentane	0.07	0.07	0.15	0.05
Methylacetylene	0.05	0.07	0.01	0.15
1,3butadiene	5.47	5.82	7.35	7.26
H_2	0.30	0.31	0.29	0.30
Total	61.00	60.60	65.64	64.83

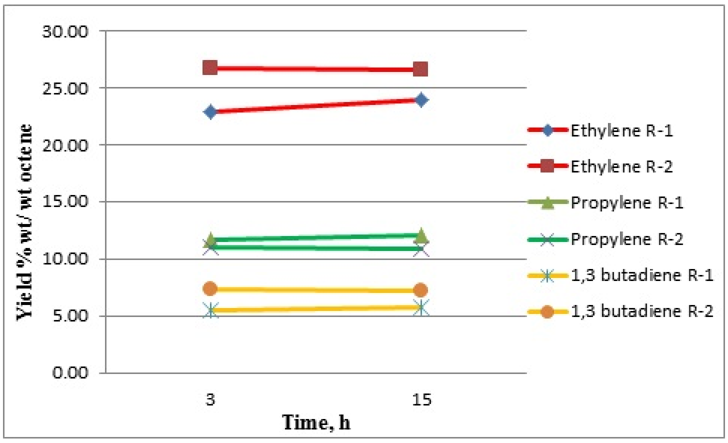

Figure 4.11: Yield pattern of major components from Octene Cracking.

4.6 Effect of Coking Rate on Run length of Reaction

To study the effect of coking rate on run-length total seven experiments were performed on bench scale cracking unit with same run conditions as shown in Table 4.13. Steam dilution ratio 0.5 (kg of steam/kg of Naphtha), at atmospheric pressure at temperature 810℃. Run time was in the range of 1-48hrs. After each run spalled coke and surface coke was measured, depending upon these values total coke formed in each run was calculated. Table 4.14 shows amount of total coke formed also coking rate. Calculation for coking rate is presented in Appendix.

Table 4.13: Run Conditions for Naphtha feed.

Run No.	1	2	3	4	5	6	7
Run time, hrs.	1	4	8	12	24	36	48
Naphtha flow rate, g/h	64.19	64.19	64.19	64.19	64.19	64.19	64.19
Water flow rate, g/h	32.09	32.09	32.09	32.09	32.09	32.09	32.09
Ratio	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Residence time, s	0.40	0.40	0.40	0.40	0.40	0.40	0.40
COT, ℃	810	810	810	810	810	810	810
Feed, wt%							
n-paraffins	32.84	32.84	32.84	32.84	32.84	32.84	32.84
i-paraffins	31.73	31.73	31.73	31.73	31.73	31.73	31.73
Olefins	1.81	1.81	1.81	1.81	1.81	1.81	1.81
Naphthene	25.94	25.94	25.94	25.94	25.94	25.94	25.94
Aromatics	7.69	7.69	7.69	7.69	7.69	7.69	7.69
Reactor MOC	Incoloy 800HT	Incoloy 800HT	Incoloy 800HT	Incoloy 800HT	Incoloy 800HT	Incoloy 800HT	Incoloy 800HT

Surface coke and spalled coke formed in each run is given in table 4.15. Spalled coke was in the range of 7.7-4.2 g. While surface coke was in the range of 0.28-0.18. Detail values of each run are given below in table 4.15. Maximum amount of spalled coke 7.7215g was obtained in run no. 4, while surface coke 0.284g maximum in case of run no. 1. Figure 4.12 shows effect of coking rate on run-length. Initially higher coking rate 33.9064 mg/cm^2h) observed. From 1-20hrs of run much impact was observed on run-length. As Ni, Cr, Fe and their oxides in coils promote catalytic coke formation initially. Once layer of catalytic coke is deposited, further lesser effect of coke was observed and then constant coking rate after 14 hrs of run.

Table 4.14: Amount of coke formed during each Runs.

Run No.	**Run Time Hrs.**	**Spalled Coke, g**	**Surface Coke, g**	**Coke Inside Coil g**	**Total Coke Formed, g**	**Coking Rate** (mg/cm^2h)
1	1	4.2830	0.2840	0.6816	5.2480	33.9064
2	4	6.3310	0.2800	0.6714	7.2920	8.9624
3	8	4.9250	0.1705	0.4088	5.5043	3.4221
4	12	7.7215	0.2790	0.6690	8.6695	4.0982
5	24	4.2300	0.1873	0.4491	4.8664	1.3105
6	36	5.4160	0.2323	0.5570	6.2053	1.1294
7	48	5.0207	0.2754	0.6604	5.9565	0.6177

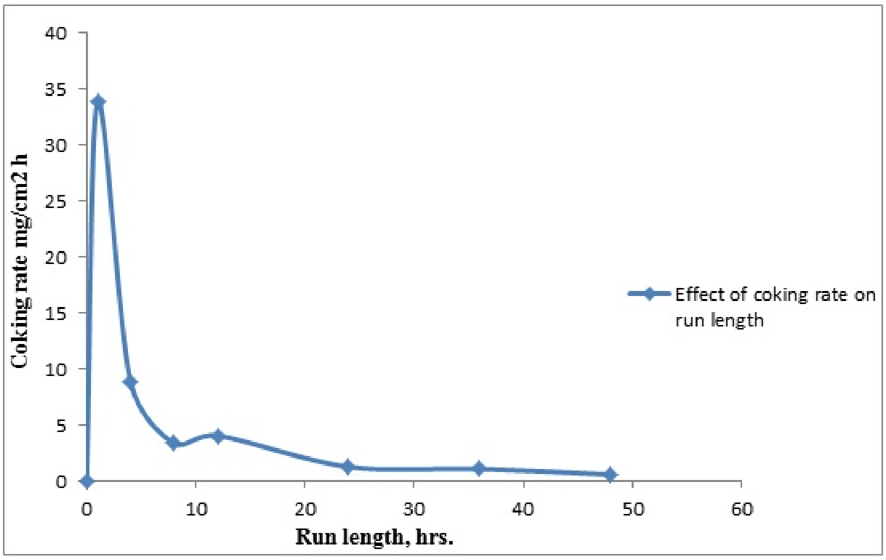

Figure 4.12: Effect of coking rate on run length of Reaction

4.7 SPYRO Model

SPYRO Simulates the cracking process inside the radiant coils of steam pyrolysis furnace of Ethylene plant as well as Transferline Exchangers, Convection section, Firebox and steam system. The software allows accurate predictions of yield patterns for feed stocks ranging from gases to gas-oil at all current operating conditions. In Table 4.15 feed conditions used for simulation of different hydrocarbon feed stocks in SPYRO Model is presented.

- Model has 128 components, more than 3000 reactions.

- Effluent specification is predicted on basis of :-

1. Feed Specification.
2. Operating conditions.
3. Geometry Specification.

- 70% world ethylene production producers use SPYRO.
- SPYRO is mechanistic model, in which basic kinetic data is used for kinetic model and model is tuned using experimental data.
- It is equation based flow sheet oriented program for simulation and optimization.
- It enables optimization of coil selection, coil sizing against yields, run-length, feed stocks flexibility, operating cost, Investment cost.

Table 4.15: Feed conditions for simulation in SPYRO Model.

Coil outlet Temperature (COT℃)	810
Cross-over, ℃	600
Ratio	0.4
Hydrocarbon flow rate, kg/hr	350
Coil Outlet pressure, Kgf/cm^2	2.4
Residence Time, s	0.2178

Figure 4.13 shows yields of Ethylene, Propylene and 1-3 Butadiene. For these feed conditions as stated in above Table, n-pentane yields maximum Ethylene, iso-butane yields maximum Propylene, and 2- Butene yields maximum 1-3 Butadiene.

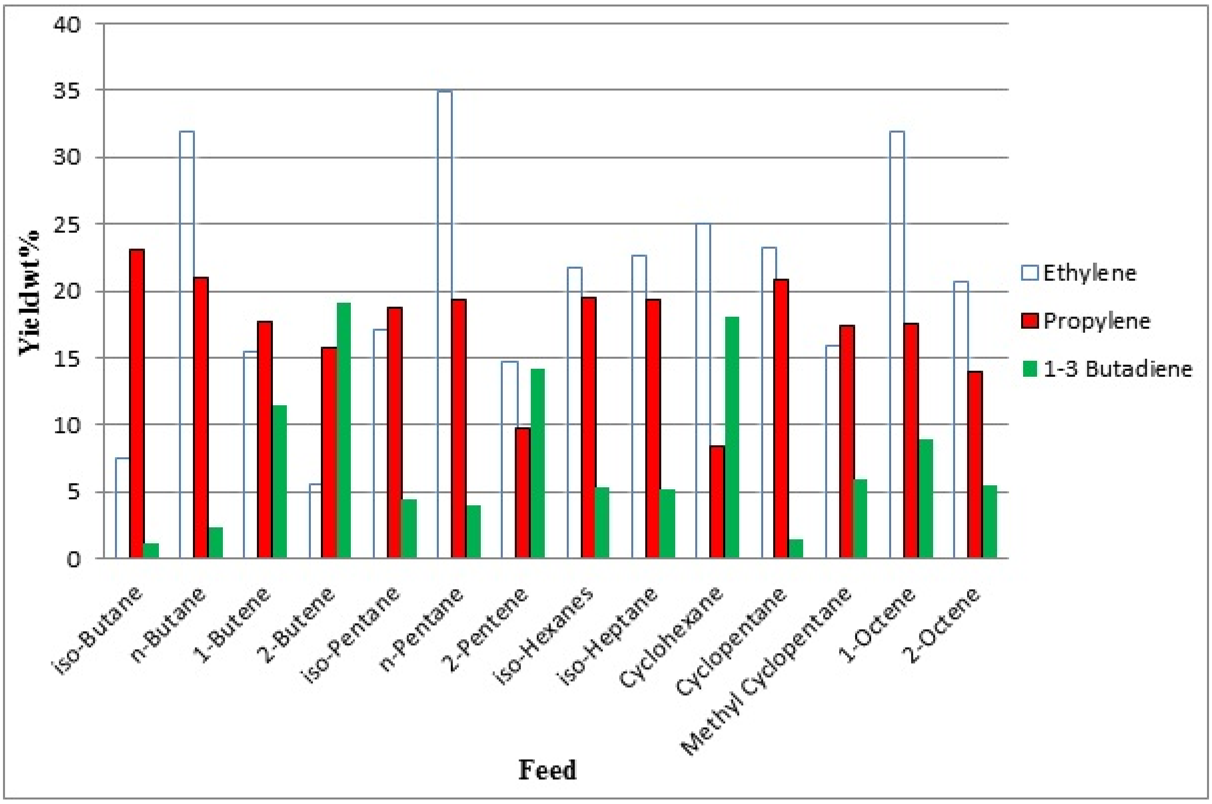

Figure 4.13: Yields from various feed stocks simulated in SPYRO Model.

Chapter 5

Summary and Conclusions

The objective of this project is to evaluate various feed stocks in bench scale cracker and optimize the process parameters to maximize yields of desired olefins. Olefins are basic feed stocks for petrochemical Industry. Operating parameters such as residence time, steams to hydrocarbon ratio, coil outlet temperature (COT) were varied over a wide range for different and unconventional feed stocks to achieve the aforementioned objective.

The various feeds considered in the present investigation includes ethane, conventional naphtha mixed with recycle C5 stream which contains 3-4% olefins and the one that is cracked in commercial plant, cyclohexane for naphthenic model component, mixed octene feed for olefinic feed stock, synthetic feed from hydrotreated naphtha without any sulfur content to study the effect of sulfur from different sulfur components like DMDS and DEDS apart from inherent sulfur in naphtha from mixed sulfur source.

Cracking of Ethane, Naphtha, Cyclohexane, Mixed octenes, Mixed hydrocarbon were carried out. For Ethane cracking the maximum yields of olefins was obtained at conditions: Ethane flow rate: 44.66 g/hr, Ratio: 1, Residence time: 0.25s, COT: 850℃. With increasing COT, coke formation also increased. The optimized feed conditions for Naphtha are: Naphtha flow rate: 65.069 g/hr, Ratio: 0.35, Residence time: 0.5s.

Addition of DMDS was found to be more effective to mixed hydrocarbon feed as coke formed was lesser compared to addition of DEDS. Cyclohexane cracking was performed with objective to study the effect of naphthenic feed on olefins specifically 1-3 Butadiene yield. At Cyclohexane flow rate: 52.16 g/hr, Ratio: 0.5, Residence time: 0.5s, COT: 790℃, 11.40 wt% 1-3 Butadiene was obtained. Similarly on same unit mixed octene cracking was also performed/ Several runs were carried out to test effect of sulfur additives such as DMDS and DEDS in terms of reduction in coke formation and olefins yield. Ethylene, propylene yields obtained are 26.52 wt%, 12.04 wt%.

Effect of run length of reaction on coke formation rate was studied. It was observed that initially coking rate is very high then reduces which further becomes steady which is known as asymptotic rate.

SPYRO model has been used to predict yields from various feed stocks with different composition in a commercial furnace. The process conditions were optimized by SPYRO simulations before going for bench scale cracker experimentation.

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Appendix A

Calculation of Flow Rates

PV = NRT
N/V = P/RT (moles/cm^3)
P= 1atm, R= 82.05746 cm^3 atm K^{-1} mol^{-1},
T= 1083 K
Substituting the values in the above equation,
we get N/V= 1.1253*10^{-5} moles/cm^3

Dimensions of the Reactor:

Inner diameter of the coil = 1.1 cm,
Height = 36.5 cm Hence,
Volume of the reactor coil = 34.701 cm^3 = Vr

Dimensions of the thermowell:

Outer diameter = 0.654 cm,
Length = 33.96 cm
Hence, volume of thermo well, Vt = 11.413 cm^3
Effective Volume for the Reaction, V = (Vr -Vt) = (34.701-11.413) = 23.288 cm^3
Residence time, t = 0.4 s
V/t = 58.22 cm^3/s

Let flow rate of naphtha and water be ‘x’ g/s and ‘y’ g/s respectively.
As the dilution ratio = 0.5,
y = 0.5x
Density of naphtha = 0.69 g/cm^3
Density of water = 1 g/cm^3
Molecular weight of naphtha = 86.4684
Molecular weight of water = 18

Naphtha flow rate = x/86.4684
= 0.01156x, mol/s

Water flow rate = y/18 = 0.5x/18
= 0.02778x, mol/s

Total flow in reactor, N, mol/s = 0.03934x

Hence, N * t/V = 0.03934x/58.22 = $6.75712*10^{-4}$x = $1.1253*10^{-5}$
Hence x = 0.017830 g/s or
x = 64.19 g/h = Flow rate of naphtha
y = 32.09 g/h = Flow rate of water

Appendix B

Yield Calculations

Feed : Naphtha +Water
Coil Outlet Temperature (COT): 810ºC
Dilution Ratio : 0.5 (Steam/Naphtha) (kg/kg)
Naphtha Flow Rate : 64.19 g/hr.
Water Flow Rate : 32.09 g/hr.
Pressure : 1 atm.
Run Duration : 48 hours.
Material Balance Calculations for Run No.1, Flow Rate Data

Table B.1: Run No. 1 Flow Rate Data

Gas, l	38	36.24	41.93	40.05	38.26
Naphtha, g	64.19	64.19	64.19	64.19	64.19
Water, g	32.09	32.09	32.09	32.09	32.09
Liquid, g	39.85	41.05	42.05	43.29	42.60

For Methane,
Mol. Wt. = 16
wt. % (FID) = 13.87%
Apparent Moles = 13.87/16 = 0.87,
Total Moles = 3.24
Apparent Mole% = 0 .87/3.24 = 26.77%
H_2 mole% = 15.69%
Actual Mole%
= 0.84*26.77
= 22.5%
wt. of methane
= 22.5*16

= 360.73

Total wt. of all the Components = 2636.3
Wt. % = (360.73/2636.3)*100
= 13.7 %

Wt.of gas in gms = (volume of gas in m^3)*(density of gas in kg/m^3)*1000
= 0.04005*1.05*1000
= 42.05gms

Yield = [(%wt of methane* wt of total gas in gms)/ (wt of naphtha in gms)]*100
= (13.7*42.05)/64.19
= 9.05 %wt/wt Naphtha.

Table B.2: Material Balance Data for R-1 (MB 4).

Component	**Mol. Wt**	**Wt.% (FID)**	**Apparent moles**	**Apparent mole%**	**Actual mole%**	**Wt.**	**Wt.%**	**yield (%wt./wt. Naphtha)**
CO	28	-	-	-	0.044	1.232	0.05	0.03
CO2	44	-	-	-	0.061	2.684	0.1	0.07
Methane	16	13.87	0.87	26.77	22.5	360.7	13.7	9.05
Ethane	30	3.46	0.11	3.56	3	89.98	3.41	2.26
Ethylene	28	36.04	1.29	39.75	33.5	937.3	35.6	23.51
Propane	44	0.51	0.01	0.360	0.3	13.26	0.5	0.33
Propylene	42	22.95	0.55	16.88	14.2	596.8	22.6	14.97
Isobutane	58	0.35	0.01	0.187	0.16	9.102	0.35	0.23
n-butane	58	0.22	0.00	0.117	0.1	5.721	0.22	0.14
Propadiene	40	0.33	0.01	0.255	0.21	8.582	0.33	0.22
t-2-butene	56	0.80	0.01	0.441	0.37	20.80	0.79	0.52
1-butene	56	3.91	0.07	2.156	1.82	101.6	3.86	2.55
i-butene	56	3.87	0.07	2.134	1.8	100.6	3.82	2.52
cis-2-butene	56	0.62	0.01	0.342	0.29	16.12	0.61	0.40
i-pentane	72	0.16	0.00	0.069	0.06	4.161	0.16	0.10
1,2-butadiene	54	2.91	0.05	1.664	1.4	75.68	2.87	1.90
n-pentane	72	3.38	0.05	1.45	1.22	87.90	3.33	2.21
Methyl acetylene	40	0.38	0.01	0.293	0.25	9.882	0.37	0.25
1,3-butadiene	54	6.24	0.11	3.569	3.01	162.2	6.16	4.07
H2	2.01				15.69	31.62	1.2	0.79
Total	-	100	3.24	100	100	2636.	100	66.13

Coke Rate Calculations

For Run no. 1: (Effect of run time on coking rate)

Surface area of Thermowell : 51.877 cm^2
Reactor inner surface area : 124.407 cm^2
Surface coke on thermowell = 0.284g
Spalled coke = 4.283g

$$Coke\ on\ reactor\ inner\ surface = \frac{(reactor\ inner\ surface\ area)*(surface\ coke\ on\ thermowell)}{(surface\ area\ of\ thermowell)}$$

Surface coke on reactor inner surface = 0.6816g

Total coke formed = Surface coke+Surface coke on reactor inner surface+Spalled coke

Total coke formed = 5.24806g

Total surface area= Surface area of Thermowell + Reactor inner surface area

Total aurface area= 176.284 cm^2

$$Coking\ rate\ (mg/cm^2h) = \frac{(Total\ coke\ formed)}{(Total\ surface\ area)*(Run\ Time)}$$

Therefore,

Coking Rate = 33.9064 mg/cm^2h.