A
PROJECT REPORT

ON

MODELLING AND SIMULATION

OF

CRACKING PROCESS

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(HEMENDRA KHAKHAR)

CERTIFICATE

THIS IS CERTIFY THAT MR. **HEMENDRA M. KHAKHAR** , MT (PROCESS) OF GAS CRACKER UNIT HAS UNDERGONE THE PROJECT AS A PART OF PARTIAL FULFILLMENT OF THE REQUIREMENT OF MANAGEMENT TRAINING ON “ **MODELLING AND SIMULATION OF CRACKING PROCESS**” UNDER MY GUIDANCE.

I WISH HIM ALL THE BEST FOR HIS FUTURE

(G.R. NANDAGOPALAN)

SR. PRODUCTION MANAGER,

GAS CRACKER UNIT,

IPCL (GPC), DAHEJ

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INTRODUCTION

Thermal cracking of hydrocarbons produces various olefins like ethylene, propylene , butadiene which are the basic raw materials for petrochemical products plastics, synthetic fibre, synthetic rubber, detergent and many organic chemicals. During pyrolysis ethylene is the major product together with significant amount of methane, proppylene, butenes, butadiene. In addition hydrogen, gasoline, fuel oil are also produced in lesser amount. The product yield depend on various factors such as residence time, temperature, partial pressure. high olefin yield favoured at high temp., low partial pressure and low residence time.

The feedstock for cracking vary widely and range from light saturated hydrocarbons such as ethane, propane to heavier petroleum cuts such as light atmospheric gas oil to vacuum gas oil . In this respect, the situation is clearly in favour of light hydrocarbons in united states, a country that is rich in natural gases containing methane as well as ethane and propane. In Europe, Japan and India by contrast naphtha traditionally supply cracker feedstocks. Following table gives worldwide picture about cracker feedstock.

FEEDSTOCK	WESTERN EUROPE	UNITED STATES	JAPAN	WORLD
ETHANE	8.0	57.5	-	30.5
LPG	11.0	19.0	7.5	11.0
NAPHTHA	69.0	9.5	92.5	49.0
GAS OILS	12.0	14.0	-	8.5
MISC.(COAL DERIVED GAS)	-	-	-	1.0

There are various licensors worldwide which offers different process configurations and major design emphasis on reaction furnaces.

(1) Lummus crest limited
(2) Stone and Webster Engg. Corporation
(3) M.W.KELLOG
(4) Linde
(5) B & RB
(6) KTI

GAS CRACKER AT GANDHAR COMPLEX:

FEEDSTOCKS

C2/C3 FEED

This feedstock is expected to be bone dry. Initially approximately 450000 MTA of c_2c_3 feed will be available . Over a period of time, the ethane content in C_2/C_3 feedstock is expected to vary. The plant has therefore been designed to handle two specific compositions of the C_2/C_3 feed namely

COMPONENTS	I (WT %)	II (WT. %)
METHANE	0.5	0.5
ETHANE	60	70
PROPANE	36.3	26.3
BUTANES	3.0	3.0
C5S AND HEAVIERS	0.2	0.2
CO2(MAX)	300PPM	300PPM

Thus the plant can handle any range of C_2/C_3 feedstock composition within the above specified compositions.

With the supply of 450000 MTA of C_2/C_3 feed ethylene production of 300000 MTA or more can be expected. When the C_2/C_3 supply is increased to approximately to 600000 MTA Ethylene production of 400000 MTA can be achieved . If C_2/C_3 feedstock is not available in sufficient quantity , additional propane cracking is envisaged.

LPG FEED

It is expected that several years later there may be shortfall in the availability of C_2/C_3 feedstock for a few years. It is then expected that C_2/C_3 will then be augmented with approximately 215000 MTA of C_3/C_4 LPG so that production of 300000 MTA of ethylene can be sustained. The source of availability of such LPG is left open, and storage and handling facilities for this LPG will have to be provided in future. Except H-10 all other furnaces are hooked up with LPG feed.

DESIGN CASE DEFINITIONS

The gas cracker plant has been designed to handle the feedstocks described above to produce 400000 mat of ethylene and 80000 MTA of propylene. However to meet this objective with different feedstock's the sizes of various equipment will vary depending on the quantities and compositions of the feedstocks. Four design cases have been selected to check the equipment for adequate sizing.

CASES FOR CRACKER PLANT DESIGN

CASE 1 (DESIGN CASE)
(MAXIMUM PROFITABILITY DESIGN CASE FOR PROCESS GUARANTEES)

When cracking the design C_2/C_3 feedstock shown in above table the ethylene plant produce 400000 mat of polymer grade ethylene. In this mode of operation , C_2/C_3 feedstock is prefractionated into a C_2 and a C_3 stream and is then separately cracked. The C_2 stream is cracked at 65% conversion and c3 stream at 79% conversion.

COMPONENT	ETHANE		PROPANE	
	MOL %	WT. %	MOL %	WT. %
HYDROGEN	36.43	3.88	17.36	1.485
METHANE	5.72	4.87	27.81	19.027
ACETYLENE	0.24	0.332	0.39	0.433
ETHYLENE	34.91	52.058	27.09	32.44
ETHANE	21.32	34.06	2.39	3.06
MAPD	0.07	0.14	0.26	0.445
PROPANE	0.45	1.05	11.07	20.83
PROPYLENE	0.03	0.067	10.74	19.23
BUTADIENE	0.47	1.01	0.86	1.50
OTHER C4	0.16	0.9	0.39	1.493

CASE 2 (CHECK CASE)

Ethylene plant processes sufficient C_2/C_3 feedstock of the alternate composition shown in above table. In this operation C_2/C_3 will be prefractionated into C_2 and C_3 and separately cracked. The c_2 c_3 stream is cracked at 55% conversion and C_3 at 90% conversion.

COMPONENT	ETHANE		PROPANE	
	MOL %	WT. %	MOL %	WT. %
HYDROGEN	33.6	3.443	17.49	1.632
METHANE	3.67	3.009	31.41	23.451
ACETYLENE	0.17	0.226	0.59	0.7158
ETHYLENE	32.54	46.99	29.81	38.96
ETHANE	29.05	44.65	3.1	4.339
MAPD	0.04	0.081	0.44	0.82
PROPANE	0.19	0.4283	8.47	17.39
PROPYLENE	0.04	0.086	4.66	9.132
BUTADIENE	0.37	0.9	1.06	1.70
OTHER C4	0.15	0.478	0.3	1.354

CASE 3 (DESIGN CASE)

The details of this mode of operation are the same as in case 1 except that the composition of c2/c3 feedstock is in accordance with the alternate composition shown in above table

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COMPONENT	ETHANE		PROPANE	
	MOL %	WT. %	MOL %	WT. %
HYDROGEN	36.53	3.92	17.11	1.38
METHANE	5.42	4.66	27.93	18.1
ACETYLENE	0.24	0.335	0.36	0.38
ETHYLENE	34.99	52.64	26.95	30.56
ETHANE	21.48	34.62	2.68	3.256
MAPD	0.07	0.14	0.24	0.33
PROPANE	0.43	1.01	11.12	19.81
PROPYLENE	0.03	0.668	10.44	17.76
BUTADIENE	0.46	1.1	0.87	1.35
OTHER C4	0.16	0.76	0.42	1.4

CASE 4 (CHECK DESIGN CASE)

The ethylene plant is designed to crack 280000 mat of C_2/C_3 feedstock of alternate composition shown in table above. In addition to above a sufficient quantity of c3/c4 feed of composition shown below cracked so as to produce a total of 300000 mat of polymer grade ethylene. In this mode of operation the C_2/C_3 feedstock is prefractionated into a C_2/C_3 and separately cracked . The C_2 stream is cracked at 55% conversion and C_3 at 93% conversion. The C_3/C_4 is cocracked at high conversion which corresponds to 93% on propane and 98% on c4 so as to maximize the ethylene yield.

COMPONENT	ETHANE(WT. %)		LPG (WT. %)	
HYDROGEN	33.66	3.449	16.75	1.588
METHANE	3.67	3.009	35.03	26.58
ACETYLENE	0.17	0.2264	0.73	0.9
ETHYLENE	32.54	46.68	28.45	37.78
ETHANE	29.05	44.65	3.01	4.283
MAPD	0.04	0.081	0.73	1.385
PROPANE	0.19	0.4283	7.62	15.9
PROPYLENE	0.04	0.086	1.85	3.68
BUTADIENE	0.37	0.90	1.27	3.5
OTHER C4	0.15	0.47	1.7	3.78

CASE 8

The ethylene plant is designed to crack 410000 MTA of $C_2/\ /C_3$ feed of design composition as shown in above table . In addition to above sufficient quantity of propane is cracked to produce 400000 MTA ethylene .

MECHANISM OF CRACKING PROCESS

Pyrolysis reaction of hydrocarbons mainly proceed via free radical mechanism. Although, some pure molecular species reactions takes place parallelly. Steam cracking of ethane feed consists of total 45 number of reactions in which 7 molecular species and 10 radicals are involved. For different feeds following summary has been given for molecular species and radicals.

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SR. NO.	COMPONENT	MOLECULAR SPECIES	RADICALS	NO.OF REACTIONS
1.	ETHANE	H_2=CH_4,C_2H_2,C_2H_4,C_2H_6, C_3H_6, C_3H_8, C_4H_6, 1-C_4H_8,N-C_4H_{10},C_5+	H.,CH_3.,C_2H_3.,C_2H_5.,C_3H_5.,1-C_3H_7.,C_4H_7.	45
2.	PROPANE	H_2,CH_4,C_2H_2,C_2H_4,C_2H_6, C_3H_6,C_3H_8,C_4H_6,1-C_4H_8,N-C_4H_{10},C_5+	H.,CH_3.,C_2H_3.,C_2H_5.,C_3H_5.,1-C_3H_7.,2-C_3H_7.,C_4H_7.,1-C_4H_9.,2-C_4H_9.,C_5H_{11}.	80
3.	BUTANE	H_2,CH_4,C_2H_2,C_2H_4,C_2H_6, C_3H_6,C_3H_8,C_4H_6,1-C_4H_8,N-C_4H_{10},C_5+	H.,CH_3.,C_2H_3.,C_2H_5.,C_3H_5.,1-C_3H_7.,2-C_3H_7.,C_4H_7.,1-C_4H_9.,2-C_4H_9.,C_5H_{11}.	76

The elementary reactions of the pyrolysis reactions are analogous for different feeds. So a classification is made which is illustrated as follows.

SR. NO.	REACTION TYPE
1.	CHAIN INITIATION REACTIONS UNIMOLECULAR: R--R' --> $R^{\cdot}$ + $R'^{\cdot}$ (EX. C_2H_6 --> $2CH_3^{\cdot}$) OR BIMOLECULAR (R'H IS AN UNSAT. HYDROCARBON): RH + RH' --> $R^{\cdot}$ + $R'H^{\cdot}$ (EX. C_2H_6 + C_2H_4 --> 2 $C_2H_5^{\cdot}$)
2.	HYDROGEN ABSTRACTION (METATHETICAL) REACTION $R^{\cdot}$ + R'H --> RH + $R'^{\cdot}$ (EX. $CH_3^{\cdot}$ + C_2H_6 --> CH_4 + $C_2H_5^{\cdot}$)
3.	RADICAL DECOMPOSITION REACTIONS $R^{\cdot}$ --> RH + $R'^{\cdot}$ (EX. n-$C_3H_7^{\cdot}$ --> C_2H_4 + $CH_3^{\cdot}$)
4.	RADICAL ADDITION REACTIONS TO UNSATURATED MOLECULES $R^{\cdot}$ + R'H --> $R''^{\cdot}$ (EX. $CH_3^{\cdot}$ + C_2H_4 --> n-C_3H_7)
5.	CHAIN TERMINATION REACTIONS BY RECOMBINATION OF RADICALS: $R^{\cdot}$ + R' --> R--R' (EX. $CH_3^{\cdot}$ + $C_2H_5^{\cdot}$ --> C_3H_8)

	BY DISPROPORTION OF RADICALS: $R^{\cdot} + R'^{\cdot}$ --> RH + R”H (EX. $CH3^{\cdot} + C_2H_5^{\cdot}$ --> C_3H_8)
6.	PURELY MOLECULAR REACTIONS RH + R’H --> R”H + R”’H e.g. “FOUR CENTER” CONCERTED REACTIONS (EX. C_2H_6 --> $C_2H_4 + H_2$) “ SIX CENTER” CONCERTED REACTIONS (EX. PENTENE-1 --> $C_2H_4 + C_3H_6$ HEXADIENES 1-3 --> HEXADIENES 2-4 ISOMERISATION) DIELES ALDER TYPE DISSOCIATION (EX. CYCLOHEXANE --> $C_2H_4 + C_4H_6$)
7.	RADICAL ISOMERISATION REACTIONS $R'^{\cdot}$ --> $R''^{\cdot}$ (EX. $CH_3CH_2CH_2CH_2^{\cdot}$ --> $CH_3CH_2C^{\cdot}HCH_3$

The basic reaction governing the cracking of ethane consists in the cracking of a saturated aliphatic hydrocarbon into a paraffin and an olefin. This is called primary cracking. By secondary cracking reactions, the entities thus formed give rise, at various points of their hydrocarbon chain, to a number of light products, rich in olefins, whose composition and yield depend upon the operating conditions selected.

Reactions achieving the more through dehydrogenation of olefins directly produced by cracking provide highly unsaturated compound, such as olefinic streams or diolefin derivatives, which display pronounced chemical reactivity. In fact, the latter react in the reverse direction to cracking and give rise to heavy products by the diels and alder reaction or cycloaddition.

The compounds thus formed, if subjected to subsequent intense dehydrogenation, are capable of producing a number of aromatic hydrocarbons and particularly benzene. These constitute the natural pasty or solid state, are designated by the general names to tars and coke. This product can in no way be compared with graphite; this is because, although it is rich in carbon, its hydrogen content is still substantial and variable, depending upon the feedstock and the operating conditions.

Whereas the cracking reaction rate becomes significant above 700 ^{o}C, dehydrogenations only take place substantially above 800 to 850 ^{o}C. Moreover, the processes of the formation of polyaromatic hydrocarbons and coke only occur rapidly at temperatures above 850 ^{0}C. The adoption of long residence time or the elevation of the reaction temperature hence favors the reaction yielding heavy aromatic derivatives at the expense of the production of light olefins by cracking.

As for the polymerisation of unsaturated aliphatic compounds, due to their high intrinsic reactivity, their polymerisation is extremely rapid, even at low temperature.

However, since these reactions represent the reverse of cracking, they are not favored from the thermodynamic standpoint in the operating conditions of pyrolysis.

As a rule, with respect to the actual steps in cracking, the reactivity of the hydrocarbons increases with the number of carbon atoms, in each family. For a given number of carbon atoms, paraffins also exhibit higher reactivity than alkylnaphthenes but lower than that of olefins.

This fact that the pyrolysis reaction proceed by a free radical and a chain mechanism were pointed out by F.O.RISE. Initiation takes place by the homolytic scission of a c-c bond with the production of free radicals. These give rise to the reaction chain by extracting a hydrogen atom from the hydrocarbon and by forming a new free radical..

Considering the simple case of ethane, the ethyl radicals are obtained by attacking ethane by methyl radicals. The ethyl radicals are stabilised by supplying ethylene and a hydrogen radical, and the reaction continues in this manner. Through this mechanism, a single methyl radical can initiate the conversion of large quantities of ethane to ethylene and hydrogen. In fact, the radicals disappear in a number of so called termination reactions, which culminate the stoppage of the chain. Whenever a new termination reactions which culminate in the stoppage of the chain. Whenever a new chain is initiated, a methane molecule is formed. Hence the pyrolysis of ethane produces hydrogen, methane and ethylene as primary products.

CRACKING REACTION MECHANISMS:

Due to production of free radicals, pyrolysis reactions exhibit pronounced sensitivity to the geometry of the reactor, and the walls tend to favor the recombination of atoms and intermediate light radicals.

GENERAL REACTION CHARACTERISTICS:

For ethane pyrolysis, a major portion of the reaction is described by a single stoichiometric equation , which is the decomposition of ethane to give ethylene and hydrogen.

For a priori understanding, models based on the elementary free radical mechanism are employed. Experimental data are used to confirm rate parameters and the basic mechanism. Because the free radical steps are mechanistic, they offer theoretical significance. An outstanding characteristic of free radicals is that their reactions are fast. Sometimes close to gas phase collision frequency. For this reason, a pseudo-equilibrium concentration is obtained quickly. The level is mostly dependent on temperature.

There are three general classification of homogeneous reactions involving the various free radicals.

1. SCISSION AND COUPLING:

Scission of a molecule introduces a pair of free radicals. High activation energy is characteristic, thus the pyrolysis requirement of high temperature. Coupling is the reverse reaction and zero activation energy is characteristic. To a large extent, these two of reactions dictate the total pseudoequillibrium radical concentration as a function of temperature.

2. HYDROGEN ABSTRACTION:

Here, a free radical abstracts hydrogen from the molecular species. The result is that the original free radical becomes a molecule, and the original molecule becomes a free radical. The reverse reaction is similar . Low, but not zero activation energies are characteristic, the reactions are relatively fast as indicated by their high frequency factors. These reactions adjust and maintain the pseudoequillibrium distribution of various free radicals.

3. DECOMPOSITION AND ADDITION:

Unimolecular decomposition of free radical results in an olefin and a smaller radical often hydrogen radical. Activation energy is normally 30-40 kcal/mol . Addition of a small radical to olefin results is 1-2 kcal/mol for hydrogen radical addition and 7-9 kcal/mol for methyl radical addition. The forward decomposition reaction is responsible for conversion to olefin and the reverse addition reaction is responsible for inhibition.

BYPRODUCT REACTIONS:

A by-product from the ethane cracking is pyrolysis gasoline, which is mixture of various aromatic hydrocarbons such as benzene and toluene plus higher paraffins, olefins and various ring compounds. Tars and coke are also formed which are highly undesirable.

THERMODYNAMICS OF CRACKING PROCESS

For optimization of operating variables, thermodynamics and equilibrium of the reactions should be well understood. The desired unsaturated structures from which they are derived at relatively elevated temperatures. The fact is illustrated by fig. Which shows the variation of the free enthalpy of formation ΔG^0 as a function of temp

Related to a carbon atom, of a number of characteristic hydrocarbon compounds. In this graph, and at a given temperature, a substance is unstable in relation to all the compounds or elements ($C + H_2$), whose representative point remains below its own, since formation from these compounds or elements requires an input energy: the substance is stable in the opposite case. Accordingly, hydrocarbons are unstable at all temperatures in relation to their elements, except for methane, which is stable at the low and medium temperatures.

Acetylene only becomes stable in relation to the simplest paraffin's at temperatures substantially above 1000 ^{o} C. The situation is more favorable for unsaturated hydrocarbons with lower energy content, such as ethylene, which is stable in relation to ethane above 750^{0} C and benzene, which is favored in relation to normal hexane above 350 to 400 ^{O}C.

Given the extreme simplicity of the chemical structure of a structure of a saturated hydrocarbon, thermal activation can only cause the scission of a C-C or C-H bond. In the former case, the random scission of a C-C bond or the carbon chain- the cracking reaction produces a paraffin and an olefin.

$$C_{m+n}H_{[2(m+n)+2]} \text{ ---> } C_mH_{2m} + C_nH_{2n+2}$$

$$G_T^{0} = 75{,}200 - 142T \text{ J/mol}$$

The scission of a c-h bond gives rise to the formation of an olefin by dehydrogenation, with the same number of carbon atoms as the initial saturated hydrocarbon, as well as hydrogen:

$$C_PH_{2P+2} \text{ ---> } C_PH_{2P} + H_2$$

$$G_T^{0} = 125400 - 142T \text{ J/mol} \quad (P>4)$$

These conversions are highly endothermic and take place with an increase number of molecules, which are therefore favored in terms of thermodynamics at high temperature and low pressure.

The comparison of the energies of the C-C bond and C-H bonds also confirms that the primary act of the pyrolysis of saturated hydrocarbons resides in the scission of a C-C bond , because this process requires much less energy than that required to split a C-H bond.

EFFECT OF OPERATING VARIABLES

:

In a reactor that is the site of a thermal reaction in the gas phase, the main operating variables are temperature, which set the level of activation of the system, the residence time left to reaction mixture to evolve in the conditions selected, and the pressure and reactant content of the feedstock, which are reflected in this case by the partial pressure of the hydrocarbons.

1. COIL OUTLET TEMPERATURE

The feedstock cannot be raised to the reaction temperature instantaneously in a furnace tube. The temperature varies along the tube according to a certain profile. The change in the slope occurring around 780 ^{o}C marks the beginning of the cracking reactions, and the first part of the pyrolysis tube merely raises the hydrocarbon feedstock to the minimum temperature required by the kinetic characteristics of the conversion. In such a reactor, which features a steep thermal gradient, the temperature profile alone represents a reality that varies with each type of furnace and in accordance with the operating conditions adopted. At the industrial level, however, the effluent exit temperature is generally considered a significant indicator of the operation of the furnace.

2. SPACE TIME:

Due to existence of a high thermal gradient along a pyrolysis furnace tube, it is difficult to pinpoint the concept of residence time. A frequent solution is to define an equivalent time, which is merely the residence time required, in an isothermal reactor operating at the furnace outlet temperature, to achieve the conversion of the feedstock identical to that observed in a variables temperature tube. In the case of an isothermal reactor, feedstock conversion is related to residence time by the equation:

$$\ln (1- Xf) = k1*\Theta$$

where,

x_f = molar conversion calculated from the molar flow rates of the reactant at the reactor inlet n_r and outlet n_{rf}

k_1 = first order rate constant for the reactor operating temperature.

T = residence time given by the ratio of the reactor volume to the feedstock volume flow rate in the reaction conditions.

In the presence of a temperature gradient , the rate constant k_1, varies between the inlet and outlet of the reactor according to Arhenius law.

For liquid feedstocks on the other hand, residence time range from 0.2-0.08 sec. ,The millisecond technology developed by Kellogg and industrialized by Idemitsu petrochemical company at their chiba factory in 1985 is operating at the lowest end of that range.

The effect of space time is studied in the range of 0.13-0.3 sec. Keeping the temp. and steam dilution ratio fixed at 1073 ^{o}K and 0.8 respectively. For both C & T pyrolysis overall gas yields increased gradually with space time tending to level off at higher space times.

Depending on the stability of the hydrocarbon, and the secondary reaction yields of the various products either increased, decreased or showed a max. with increasing space time. The methane yield increased monotonically with space time, whereas ethylene yield tend to level off at the higher space times. The propylene yield showed a max.

whereas the yield of 1- butene decreased with an increase in space time. As shown in fig. With an increases in space time, more of the CO and CO_2 generated.

3. PARTIAL PRESSURE OF HYDROCARBON:

From the thermodynamic standpoint, pyrolysis reactions producing light olefins are more advanced at low pressure, a range in which the condensation reactions are highly disadvantaged. This is why, owing to the pressure drops inherent in the circulation of the reaction mix., furnace tubes operate at exit pressures close to atm. Pressure.

Moreover, the condensation side reaction rate is much more heavily influenced by the hydrocarbon content of the reaction mixture than the rate of primary reactions., which are substantially of the first order with respect to the reactants. A decrease in the partial pressure of the hydrocarbons, by the dilution with steam for example reduces the overall reaction rate, but also helps to enhance the selectivity of pyrolysis substantially in favor of the light olefins desired. Apart from this specifically kinetic role, steam exerts a number of other beneficial effects.

- Heat input during the introduction of steam into the feedstock.
- Decrease in the quantity of heat to be furnished per linear meter of tube in the reaction section.
- Contribution to the partial removal of coke deposits in furnace tubes by reaction with steam.

$$C + H_2O \underset{<--}{-->} CO + H_2$$

The use of steam also involves a number of drawbacks which impose a limit value to its content in the feedstock. Since the steam must be heated to the reaction temperature, its presence increases the reaction volume required and hence the furance investment. And its separation from the hydrocarbon effluents requires very large condensation areas and results in high utility consumption.

The amount of steam employed, which is normally expressed as the weight of feedstock, depends on the molecular weight of the hydrocarbon treated.

For a given raw material the composition of the reaction effluent is obviously related to the variables of temperature, residence time, dilution ratio. At the industrial level, the individual optimization of these parameters normally leads to contradictory requirements. Hence the solution adopted is generally the result of a compromise in the choice of furnace design on the one hand, and operating conditions on the other. However, an attempt is made to express the overall influence of these factors on the performance of the reaction section by means of the representative value that can indicate the degree of severity of the treatment.

SEVERITY CONCEPT:

In the treatment of liquid petroleum fractions with very complex composition, the degree of feed gasification is generally employed, measured by the weight yield of light products containing three carbon atoms or less.

Process licensors have tried to supply this overall assessment by a finer analysis of the severity of operation of a pyrolysis furnace operating on a coupled feed. Among the values, thus determined are the MCP for the treatment of Naphthas, based on considerations stemming from the kinetic theory of gases and developed by Wall and Witt of the Selas Corporation, and especially the KSF proposed by Zdonic of Stone and Webster Engg.

The KSF severity index is defined as a logarithmic function of the conversion of a reference hydrocarbon present in the feed. Zdonik selected n-pentane, a compound that is always present in the naphthas, and which offers the advantage that it can’t be formed in the reaction or the components by a side reaction.

MODELLING OF CRACKING PROCESS

There are three ways of approach for scaling up of cracking coils. The first direct experimental simulation is not sufficiently accurate if the conversion is to be predicted since complete similarity between industrial, pilot and bench scale unit is impossible. The second approach is based upon the equivalent space-time V_E/F_0. It is shown that for a given dilution, there is a unique relation between V_E/F_0 and conversion of hydrocarbon feed. The corresponding product distribution is obtained from graphs or correlations derived from essentially isobaric small-scale experimentation. Since, the product yield depend upon partial and total pressure and since in commercial cracking these vary along the coil, the selection of the average value for the total and partial pressure inevitably leads to some error in the predicted product distribution.

The third approach makes use of the detailed mathematical model to simulate cracking operation. The model generates the conversion, product yields, temperature and pressure profiles along the reactor. Excellent agreement between simulated and measured values is arrived at for the cracking of ethane in an industrial furnace.

MODELING AND SIMULATION APPROACH:

Simulation of a cracking coil requires integration of a set of

Continuity equations for conversion of each process gas species

$$dF_i/dz = - \Sigma (S_i r_i) * \pi * dt^2 /4$$

Energy balance

$$dt/dz = 1/ \Sigma F_i Cp_i \{ Q(Z)* \pi *dt + \pi * dt^2/4*r_i *(- \Delta Hi)$$

In order to avoid the complications of solving the above energy balance equation with the heat transfer coefficients, specific heats of each components, the heat flux profiles and heat of reaction.

We have applied directly temperature profiles being used in industrial ethane cracker across the length of the coil in a polynomial form (given in SWEC technology transfer document)

MATHEMATICAL MODELLING

The thermal cracking process can be mathematically described using the fundamental balance equations (specifically, the material balances for each molecular and radical component, the energy balance and the momentum balance). The solution of this well known set of differential equations is complicated by two specific problems.

1. Not all the initial values for the differential equations are known. (Typically, industrial data are given for the reactor inlet composition and temperature and the outlet pressure and temperature); an iterative solution method is hence required.

2. The ‘stiffness’ of the material balance equations results from the wide range of kinetic parameter values and the fact that the low radical concentrations are result of very fast formation and disappearance reactions (close to steady state); extremely small integration (time) steps and hence prohibitively long computer time would be required if usual numerical integration methods were applied.

SELECTION OF KINETICS:

For simplicity the radical reaction schemes for thermal cracking developed by SUNDARAM and FROMENT (1977) is used here. They lead to a set of continuity equations for the reacting components that are not mathematically stiff due to less difference of the orders of magnitude between the concentrations of molecular and radical species. This kinetic model was based upon a rigorous screening between several plausible molecular reaction schemes on the basis of thermodynamic considerations and statistical tests on kinetic parameters the scheme together with the kinetic parameters is given on the next page. The kinetic parameters for reverse reactions (2) and (5) have been obtained from equilibrium data.

FUNDAMENTALS OF MODELLING AND SIMULATION

The use of models in chemical engineering is well established but the use of dynamic models, as opposed to the more traditional use of steady state models for chemical plant analysis, is much more recent. This is reflected in the development of new powerful commercial software packages for dynamic simulation. Which has arisen owing to the increasing pressure for design verification, process integrity and operation studies for which a dynamic simulation is an essential tool. Induced it possible to envisage dynamic simulation becoming a mandatory condition in the safety assessment of plant. With consideration of such factors as startup, shutdown, abnormal operation, and relief situations.

Dynamic simulation can thus be seen to be an essential part of any hazard or operability study, both in accessing the consequences of plant failure and in the mitigation of possible effects. Dynamic simulation is thus of equal importance in large scale continuous process operations as in other inherently dynamic operations such as batch, semibatch and cyclic manufacturing process.

Dynamic simulation also aids in a very positive sense in gaining a better understanding of process performance and is a powerful tool for plant optimization, both at the operational and at the design stage. Furthermore steady state operation is then seen in its rightful place as the end result of a dynamic process for which rates of change have eventually zero.

The basic stages in the above modeling methodology are indicated given below.

- Define model aim
- Start simple, built in complexities later
- Use the model to learn
- Models are there to applied

GENERAL ASPECTS OF MODELLING APPROACH

1. Modeling improves understanding
2. Models help in experimental design
3. Models may be used predictively for design and control
4. Models may be used in training and education
5. Models may be used for process optimisation

GENERAL MODELLING PROCEDURE:

The third approach is concerned with the numerical methods to solve the set of equations and conditions ; for instance, general purpose or specifically conceived programs are developed to handle large system of stiff differential equations.

The main objective of the model is of course to simulate accurately the system; namely to predict the process behaviour both inside and outside the range of experimental data.

TYPES OF MODELLING:

- **EMPIRICAL MODELLING**:

The main feature here is the absence of even the simplest reaction hypothesis of course the integration of the fundamental differential equations as a function of tube length of residence time is absent. Only the overall material balance and energy balance around the unit is possible.

➢ MOLECULAR (STOICHIOMETRIC) MODELLING:

Although thermal cracking involves mainly free radical reactions, only the apparent global molecular reactions are accounted for in this approach . SUNDARAM and FROMENT (1977a) proposed for ethane and propane pyrolysis an e.g.. of discrimination of the best kinetic model between rival molecular schemes. These molecular kinetic schemes are generally drastically simplified in order to reduce the number of a rate equations to only a few global reactions.

This molecular approach has been more of less successfully applied to the pyrolysis of ethane, propane, butane and their mixtures. Adequate description of pressure loss and temperature profiles along the coil and in the metal skin is an advantage of this type of modeling over the prior one. As compared to the more mechanistic approach, the obvious advantages include a simpler formulation, shorter development time and substantial savings of computer storage and computing time.

➢ MECHANISTIC MODELLING:

Since there is now sufficient understanding and both kinetic and thermochemical data are available to describe the most complex pyrolysis in terms of a finite number of elementary step reactions, the mechanistic approach uses such complex reaction network. To handle these complex kinetic scheme at least two major difficulties have to overcome, depending upon the largeness and stiffness of the differential equations system in addition to the necessity of efficient numerical algorithms, it is also compulsory to have a chemical compiler.

SIMULATION:

INTRODUCTION

In simulation a mathematical model for a unit operation relates inputs and outputs of mass and energy to process and equipment parameters. To model a distillation column, for example, you need to relate feed streams to the product streams and to parameters such as number of trays and reflux ratio.

This model can be solved in two ways, depending upon what you know and what you want to find. In a design calculation inputs and outputs are known solving the model gives you the values of design parameters. A performance calculation determines what you would get from a set of inputs and operating conditions.

Performance calculations on individual unit operations form the basis for one method of simulation complete process- the sequential modular approaches. This method works well with models made of unit operation in series. Solving a model for the first gives output, which are inputs to the unit. Calculations move on from unit to unit to arrive at the final answer. Because only one model needs to resident at any one time, rigorous models and large problems can be solved with modest computing resources.

NUMERICAL METHOD:

The following numerical method was employed in the simulation.

FOURTH ORDER RUNGE KUTTA METHOD:

The fourth order RUNGE KUTTA method integrates and solves the set differential equations simultaneously but requires initial boundary values. You input the values of the independent variables, and you get out new values which are stepped by a stepsize ‘h’ (which can be positive or negative). The RUNGEKUTTA method treats every step in a sequence of steps in identical manner. Prior behaviour is not used in its propagation. This is mathematically proper, since any point along the trajectory of an ordinary diff. Equation can serve as an initial point. The fact that all steps are treated identically also makes it easy to incorporate RUNGEKUTTA into relatively “driver” schemes.

ODEINT:

This is special code used as driver in the simulation. A good ode integrator should exert some adaptive control over its own progress, making frequent changes in its step size. Usually the purpose of this adaptive step size control is to achieve some predetermined accuracy in the solution with minimum computational effort. Many small steps should tiptoe through treacherous terrain, while a few great strides speed through smooth uninteresting countryside.

RESULTS AND DISCUSSION

The simulation program developed in ‘**FORTRAN** ‘ predicts the product yield pattern in ethane cracking process. The kinetic model of the pyrolysis reaction developed by **SUNDARAM** and **FROMENT** is used. The solution of differential equations has been derived by **RUNGE KUTTA** fourth order and ODEINT method. This converges to values which are in agreement with design and operating yield.

SR.	COMPONENT	DESIGN YIELD	SIMULATED YIELD	OPERATING YIELD

NO.		(WT. %)	(WT. %)	(WT. %)
1.	HYDROGEN	6.05	6.10	6.23
2.	METHANE	6.258	6.53	6.21
3.	ACETYLENE	0.4558	0.39	0.581
4.	ETHYLENE	0.8265	0.803	0.79
5.	PROPANE	1.1825	1.42	1.2671
6.	PROPYLENE	0.128	0.73	1.639
7.	BD + C4	2.69	3.25	5.83

SIMULATION RESULTS:

- The depletion of ethane is exponential. Thus maximum conversion takes place near the inlet. This is due to the fact that there is maximum driving force with the presence of unconverted ethane. This leads to maximum rate of change in temp. Profile at 5-10 meter of the tube. The temperature still goes on increasing but now the slope is very less. This increase may be possibly due to coke formation. This is validated with the increasing ksf profile.

- The pressure drop is around 1.5 times the inlet pressure but with more coking it is bound to increase which is quite higher than the design pressure drop.

- Propylene goes through a maximum and the yield decreases as we approach the end of the coil. Other flowrates are not all that significant except methane buildup which increases with tubelength.

- Ethylene yield decreases with increase in ethane conversion.

For ethane:
Ethylene yield(at X = 65 %) = 0.5293/0.6537 = 80.96 %
Ethylene yield (at X = 55 %) = 0.4669/0.5535 = 84.35 %
For propane:
Ethylene yield (at X = 79 %) = 0.3244/0.7913 = 40.99 %
Ethylene yield (at X = 87 %) = 0.3896/0.8661 = 44.98 %

SIMULATION RESULTS VS. EXPERIMENTAL RESULTS:

The modelling of the tube side gives rise to a series of differential equations. We have chosen an industrial heat flux profile and therefore the simulation results should have represented near to optimum results.

- In a simulator we just take care of the operating variables and in an actual process the design variables induce some practical constraints. As coking is a major concern, the choice of material can allow us to have a higher coil outlet temperature with less coking. Coking model has not been incorporated which changes actual heat flux profile.
- The pressure drop can also vary from the experimental one due to:
- The pressure drop across the bends calculated empirically is a function of the tube geometry and other factors, which tend to be differing on site.
- The correlations used are for ideal turbulent flow which may not be uniform.
  kinetic model of sundaram and froment is based on molecular reactions which causes deviation with respect to design values.
- The viscosity changes with temperature have been neglected and a typical gas viscosity is taken.
- This model predicts yield for pure ethane feed. In our furnace ethane composition is:

Ethane:	95-96 %
Methane :	4-5 %

OPTIMISATION RESULTS:

By keeping the conversion to max. Of 65 % we found out the best KSF of the process. Keeping this KSF constant we change the input heat flux profile to maximize ethylene yield. These results can be seen in the various graphs and hence the best heat flux profile can be selected.

The number of trials can get us close to best results but the real optimisation can be achieved by defining an objective function and converging towards it.

The optimum results reflect not only ethylene maximization but also the less amount of other unwanted byproducts formed. It should correspond to a temperature and pressure which is allowable.

The best results obtained in our trial are the ones in which the heat flux profile fed near to the industry. As we change the heat flux profile we get to compromise on the yield with coking posing a very important. Thus the right balance is struck to achieve maximum economic gains.

CASE STUDY: IMPORTED PROPANE CRACKING COUPLED WITH C2/C3 CRACKING

At present, our plant is operating at 50 % capacity i.e. Two furnaces at max. Feedrate. One furnace is on ethane cracking and the other one is cracking LPG and recycle propane. The operating conditions of furnaces are given in the attached datasheet. It has been decided to incorporate propane cracking additional to present C_2/C_3 cracking. This leads to three furnace operation each having different feedstocks.

Material balance has been done for the future operation based on 500 t/hr. Of imported propane additional to C_2/C_3 feed and feed quantities has been calculated. Based on these data, product pattern and various other streams has been compared with simulated results. Due to additional propane cracking, ch4 content in dryer outlet flow increases from 13.2 % to 15.3 % which corresponds to mass flow of 11.8 t/hr. Compared to 8.1 t/hr. At present.Propylene tower hydraulic flow is 19.9 t/hr. which is at design conditions.Acetylene wt. % is 1.9 %

MATERIAL BALANCE:

Basis: 1. 500 ton/day of imported propane
2. Ethane furnace load : 24 t/hr.

SR. NO.	COMPONENT	MOL %	WT. %
1.	METHANE	1.1	0.39
2.	ETHANE	42.3	31.97
3.	PROPANE	36.7	39.05
4.	BUTANE	12.5	19.0
5.	C5+	7.4	9.65

Suppose X: fresh ethane required

Y: recycle propane

Therefore,

LPG quantity in C_2/C_3 feed = (39.05 + 19.0)*x/31.97 = 1.814*x t/hr,

Typical recycle streams at average severity:

SR. NO.	FEED	ETHANE (R.R.)	PROPANE (R.R.)
1.	ETHANE	0.4	0.005
2.	PROPANE	0.015	0.19
3.	LPG	0.04	0.159

Taking material balance around the furnace system:

Ethane balance:

X + 0.4X + 0.004(1.814X) + 0.035X (21+Y) = 24

Propane balance:

Y = 0.005 [X + 0.4X + 0.04(1.814X) + 0.159 (1.814X) + 0.19 (21 + Y)

Simplifying this equations we get,

1.47256X + 0.035Y = 23.265

0.2955X + 0.8098Y = 3.99

Solving ,

$X = 15.55$

$Y = 10.61$

RESULTS:

- LPG = 28.2 t/hr.
- C_2/C_3 = 48.3 t/hr.
- Ethane recycle = 17 t/hr.
- Fresh ethane = 15 t/hr.
- Propane recycle = 10.5 t/hr.
- Ethylene = 33.2 t/hr. (from C_2 = 12.1 t/hr., C_3 = 10.85 t/hr., C_4 = 10.25 t/hr.)
- Propylene = 8.8 t/hr.

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