PRJ, Vol. 2 (January 1990); P. 12–16, 4 FIGS, 4 TABLES.

LPG CRACKING IN AN EXISTING NAPHTHA-BASED ETHYLENE PLANT

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التكسير الحراري لغاز البترول المسال في مصنع للاثيلين قائم على النافثا

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تبحث الدراسة في إمكانية التكسير الحراري لغاز البترول المسال في مصنع قائم لإنتاج الإثيلين باستخدام النافثا . وقد مكن وضع نموذج محاكاة لحركية تكسير غاز البترول المسال من حساب نواتج التكسير تحت ظروف تشغيل متعددة ، وكذلك تقييم المكاسب الإقتصادية نتيجة إستبدال جزء من النافثا بغاز البترول المسال حسب مستوى الإستبدال المفترض . حيث أوضحت الدراسة بأن إستعمال غاز البترول المسال في بعض أفران التكسير يمكن أن يكون مربحاً في حالة توفر الهيكلية المناسبة لأسعار النواتج والمواد الخام .

ABSTRACT

This paper reports on an investigation of LPG cracking in existing naphtha-based ethylene plant. Rigorous simulation of LPG cracking kinetics permitted the calculation of product distribution under various operating conditions. The economic gains expected as a result of substituting parts of the naphtha by LPG were assessed under various levels of substitutions. The investigation shows that under favorable price structure of both raw materials and products switching some naphtha crackers to LPG can be a profitable proposition.

INTRODUCTION

The type of feedstock used in an ethylene plant has a major influence on steam cracker product slate and overall plant economics. Cracking of light feedstocks such as ethane produces the highest ethylene yield and the least amounts of co-products. Since such a plant is simple and straightforward it requires the lowest capital investment. On the other hand, because cracking of heavier feedstocks such as naphtha results in the production of large quantities of co-products, an elaborate separation section is required which is translated to higher capital investment.

In terms of flexibility, an ethylene plant based on heavy feedstock gives greater flexibility in terms of product slate compared with a plant feeding ethane only. Moreover, while significant changes both in equipment and operating conditions are required for an existing ethane-based plant to change to heavier feedstock such as naphtha [1], minor changes are usually anticipated when lighter feedstocks are introduced in a naphtha or gas oil-based plant.

Under certain conditions, co-cracking of light feedstock such as propane, butane, or both in naphtha based plant has merit. This is particularly true when the prices of light olefins such as ethylene and propylene enjoy greater margin compared with those of heavier products such as mixed C_4's and pyrolysis gasoline. The relative price of naphtha and LPG is another important factor.

The present paper reports on an investigation of LPG cracking in an existing naphtha-based ethylene plant. The investigation covers the rigorous simulation of LPG cracking in the existing naphtha cracking furnaces to predict the distribution of products at reactor outlet under various operating conditions. The economic gains expected as well as the extent of LPG substitution are also investigated.

KINETICS OF LPG CRACKING

In their simplest form, kinetic models of thermal cracking of hydrocarbons are empirical in nature. On the other hand, kinetic models based on free radical mechanisms for the cracking reactions: while fundamentally sound, can be quite complex for practical applications.

An intermediate approach used by many investigators is based on the so-called "molecular schemes"

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which are approximations to the true nature of the cracking reactions. This approach has been successfully utilized in the case of light feedstocks such as ethane, propane, butane and their mixtures [2, 3].

The kinetic model used in this investigation is based on molecular schemes of propane and butane cracking as developed by Sundaram and Froment [3]. The scheme, together with the kinetic parameters is given in Table 1.

STEAM CRACKER SIMULATION MODEL

The simulation of an industrial cracker which basically consists of long coils placed horizontally or vertically inside a fired furnace, requires the following set of component mass balance equations together with the energy equation and the pressure drop equation written for plug flow reactor:

A. Component mass balances

$$\frac{dF_j}{dz} = sr_j \tag{1}$$

with

$$r_j = \sum_i u_{ij} r_i \tag{2}$$

for

$i = 1 \ldots\ldots\ldots 11$

$j = 1 \ldots\ldots\ldots 16$

B. Energy equation

$$\frac{dT}{dz} = \frac{1}{F_t Cp_m}\left[Q(z)\pi D_t + s\sum_i \Delta H_i r_i\right] \tag{3}$$

The specific heat of the mixture follows from:

$$Cp_m = \sum_j \frac{F_j}{F_t} Cp_j \tag{4}$$

where

$$Cp_j = a_j + b_j T + c_j T^2 + d_j T^3 \tag{5}$$

$$F_t = \sum_j F_j + F_{steam} \tag{6}$$

and the heat of the reaction is the algebraic sum of the heats of formation of reactants and products:

$$\Delta H_i = \sum_j u_{ij} \Delta H_{fj} \tag{7}$$

C. Pressure drop equation

$$-\frac{dP}{dz} = \propto \left[\frac{2f}{D_t} + \frac{B}{R_b}\right] \frac{RT}{M_m P g} G^2 \tag{8}$$

In equation (8), f is friction factor in straight tubes and is defined as:

$$f = 0.046 R_e^{-0.2} \tag{9}$$

Also, B accounts for the additional pressure drop in

Table 1 Molecular Reaction Scheme for LPG Cracking

Reaction	Order	A (s^{-1} or $1.mol^{-1} \cdot s^{-1}$)	E (kcal/mol)
$C_2H_6 \rightleftharpoons C_2H_4 + H_2$	1	4.652×10^{13}	65.21
$C_3H_6 \rightleftharpoons C_2H_2 + CH_4$	1	3.794×10^{11}	59.39
$C_2H_2 + C_2H_4 \rightarrow C_4H_6$	2	1.026×10^{12}	41.26
$2C_2H_6 \rightarrow C_3H_8 + CH_4$	1	3.750×10^{12}	65.25
$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$	2	7.083×10^{13}	60.43
$C_3H_8 \rightleftharpoons C_3H_6 + H_2$	1	5.880×10^{10}	51.29
$C_3H_8 \rightarrow C_2H_4 + CH_4$	1	4.692×10^{13}	50.60
$C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_3H_6$	2	2.536×10^{13}	54.06
$2C_3H_6 \rightarrow 3C_2H_4$	1	1.514×10^{11}	55.80
$2C_3H_6 \rightarrow 0.5C_6^+ + 3CH_4$	1	1.423×10^{9}	45.50
$C_3H_6 + C_2H_6 \rightarrow 1-C_4H_8 + CH_4$	2	1.000×10^{14}	60.01
$n-C_4H_{10} \rightarrow C_3H_6 + CH_4$	1	7.000×10^{13}	54.64
$n-C_4H_{10} \rightarrow 2C_2H_4 + H_2$	1	7.000×10^{14}	70.68
$n-C_4H_{10} \rightarrow C_2H_4 + C_2H_6$	1	4.009×10^{12}	61.31
$n-C_4H_{10} \rightarrow 1-C_4H_8 + H_2$	1	1.637×10^{12}	62.36
$1-C_4H_8 \rightarrow C_6^+$	1	7.685×10^{6}	29.84

coil bends and is given by:

$$B = B'\left(0.051 + 0.19\frac{D_t}{R_b}\right) \qquad (10)$$

For 180 bends, $B' = 1.4$ [4]

Model Solution

The solution of the above set of conservation equations is accomplished numerically using fourth order Runge-Kutta method with Gill modification given the geometry of the coil and the following initial conditions ($Z = 0$):

$F_j = F_{j0}$
$T = T_0$
$P_t = P_{t0}$

Plant Investigated

The particular ethylene plant investigated is designed for naphtha feed only. The plant, with a capacity of 330,000 tons/year has ten cracking furnaces, seven for cracking naphtha, one for ethane-propane recycle cracking, and two for stand-by service. Each furnace consists of eight coils. Each coil is 73 m in length and has a diameter of 0.108 m.

The naphtha crackers are designed for total feed of 80.46 kg/m^{2}s, and steam to hydrocarbon ratio of 0.6 kg/kg of naphtha. The recycle cracker is designed for feed rate of 58.17 kg/m^{2}s, and steam to hydrocarbon ratio of 0.4 kg/kg of recycle mixture.

Simulation of LPG cracking

The steam cracker simulation model described by equations 1 through 10 was numerically integrated for the coil geometry previously described utilizing the LPG kinetic model given in Table 1 with the objective of determining suitable operating conditions that yield high amounts of light olefins, namely ethylene and propylene. This depends largely on the severity of cracking which in turn depends on such variables as flow rate, temperature, and steam to hydrocarbon ratio.

Several definitions of cracking severity are available depending on convenience. Percent decomposition of key reactant, methane analysis, propylene analysis, propylene to ethylene ratio, and methane to propylene ratio are just some of the many measures of cracking severity in common use. In this investigation, methane to propylene ratio is selected to measure the cracking severity of LPG since it is easily available and is often the best choice for this feedstock [5].

For the purpose of simplifying the analysis and at the same time insuring adequate cracking run, a steam to hydrocarbon ratio of 0.4 is selected. Consequently, cracking severity is determined by flow rate and temperature only. Several levels of cracking severity are simulated by varying mass velocity and average heat flux in the radiation section as follows:

Mass velocity, G: 80–90 kg/m^{2}s
Heat flux, Q: 18–22 kcal/m^{2}s

A total of 15 computer simulation runs were performed, the results of which are summarized in Fig. 1 As can be seen from this figure, higher ethylene yields are obtained at higher severities but at the same time the propylene yield is significantly reduced. The yields of both ethylene and propylene are sufficiently high only in the cracking severity range of 1.5–2.5. Thus, only this range is considered for further study concerning the economic merit of LPG utilization as an alternative feedstock. Six case studies are identified for the purpose as detailed in Table 2.

Economic Analysis

The economic viability of LPG cracking under the operating conditions cited in Table 2 is analysed on the following bases:

- Product distribution of the whole plant
- Price levels of both products and raw materials.

Since product distribution of the whole plant depends on the level of substitution of naphtha by LPG, three levels of substitution are considered:

	LPG	*Naphtha*
Level 1	1 cracker	6 crackers
Level 2	2 crackers	5 crackers
Level 3	3 crackers	4 crackers

The final product distribution is calculated on the

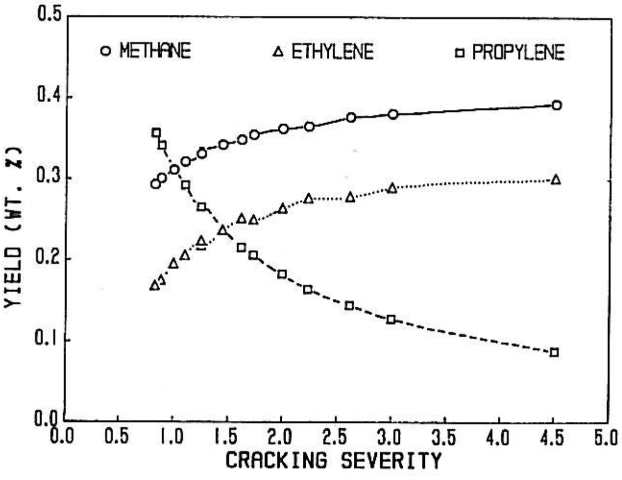

FIG. 1. Effect of cracking severity for LPG feed

Table 2 Case studies for LPG Cracking

Case No.	Flow velocity kg/m²s	Heat flux kcal/m²s
1	80	18
2	80	19
3	85	19
4	85	20
5	90	21
6	90	22

basis of the total effluent from all crackers including the ethane-propane recycle cracker.

Also, since wide variations in prices are usually observed for raw materials and products during the past few years, two sets of prices are assumed as shown in Table 3. The first price set is average prices quoted during the first quarter of 1989. This set may represent a price level that is considered favorable economically. The second price set may be taken to represent somewhat unfavorable price level.

The results of the economic analysis are summarized in Figs. 2, 3 and 4. Fig. 2 illustrates the effect of operating variables on overall plant revenue when only one naphtha cracker is switched to LPG under the first price level. It is quite evident from this figure that positive economic returns are possible in all cases. However the highest incremental profit case (case 5) is also high heat flux case. Thus, final selection among the various cases must also consider any additional operating costs involved.

The effect of varying the level of substitution of naphtha by LPG is illustrated in Fig. 3 for the first price level. The sensitivity of the substitution to the assumed price level is shown in Fig. 4 when the second price set is used in the economic analysis. As expected, this figure shows the great sensitivity of feedstock substitution schemes to prevailing market prices of both feedstocks and products.

Implications for Separation Section

Whenever a change of feedstock is considered, the effect under the new operating conditions upon the

Table 3 Price levels assumed for raw materials and products (cents/lb)

	Level I	Level II
Feedstocks		
Naphtha	7.86	5.95
LPG	5.36	5.59
Products		
Ethylene	31.0	21.6
Propylene	25.5	15.14
Mixed C4's	4.0	4.0
Pyro. Gas.	10.2	7.77

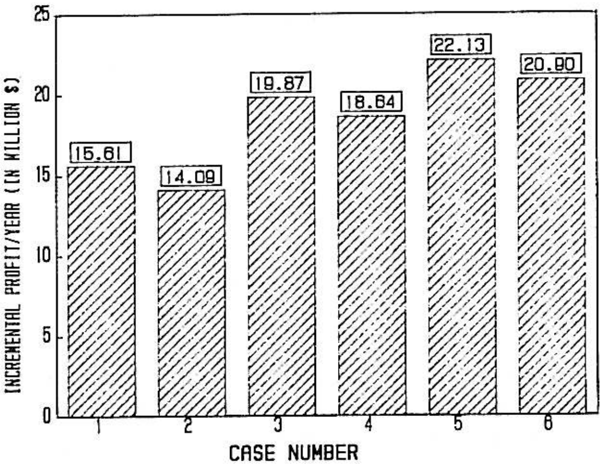

FIG. 2. Effect of operating conditions on ethylene plant revenue

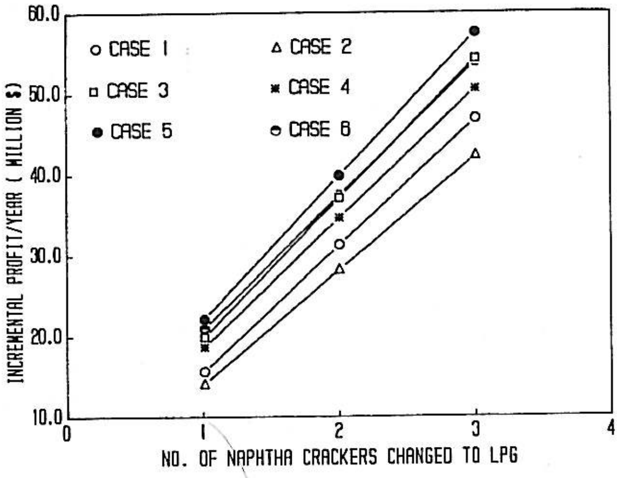

FIG. 3. Substitution level Vs. plant revenue (Price level I)

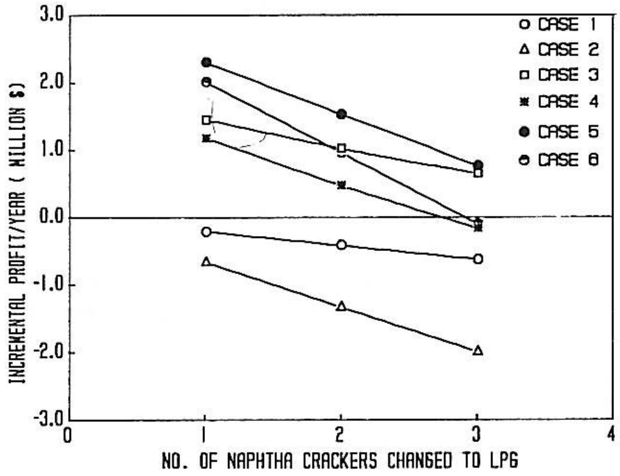

FIG. 4. Substitution level Vs. plant revenue (Price level II)

Table 4 Percent Change in Flow rate Relative to Design Case

Case No.	No. of LPG Furnaces	Quench Section	Light ends Sep. Section
5	1	2.55	5.51
	2	4.08	10.54
	3	5.62	15.57
6	1	2.55	5.01
	2	4.08	9.53
	3	5.62	14.06

separation section must be carefully assessed. Table 4 shows the results of the change in flow rates to the various parts of the separation section computed for the high mass velocity case. As can be seen from this table, flow rate increase to the quench tower is no more than 6% when three naphtha crackers are changed to LPG so that the thermodynamic and hydraulic behavior are not dramatically changed. In the case of the light ends separation section the increase in flow rate is in the range of 5–15%. This also can be considered tolerable but warrants a check on the performance of this section by means of thermal and hydraulic analysis particularly for the cases with greatest increase in flow rate.

CONCLUSIONS

An investigation of switching some naphtha cracking furnaces to LPG in an existing naphtha-based ethylene plant is performed. Rigorous simulation of LPG cracking permitted the calculation of product distribution in the reactor effluent. It was also used to determine the most suitable operating conditions for LPG cracking under existing plant conditions. In addition, the investigation shows that under favorable price structure of raw materials (naphtha and LPG) and products (ethylene, propylene, mixed C_4's, and pyrolysis gasoline), switching some of the naphtha cracking furnaces to LPG can enhance the economic returns of the existing plant. This is particularly true when the market price for naphtha enjoys a commanding lead over LPG.

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NOTATION

A	frequency factor
B	factor for pressure drop in bends
C_p	specific heat
D	internal coil diameter
E	activation energy
F_j	molar flow rate of component j
F_t	total molar flow rate
f	friction factor
G	mass flow velocity
g	acceleration of gravity
ΔH	heat of reaction
i	reaction index
j	component index
M_m	molecular weight of mixture
P	pressure
Q	heat flux
R	gas constant
R_b	radius of bend
R_e	Reynolds number
r_i	reaction rate
r_j	component reaction rate
s	coil cross sectional area
T	temperature
u_{ij}	stoichiometric coefficient of component j in reaction i
Z	distance along coil
$\propto$	conversion factor from Kgf/m^2 to atm

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