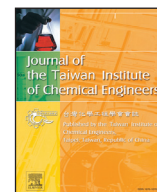




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Investigation of propane addition to the feed stream of a commercial ethane thermal cracker as supplementary feedstock

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ABSTRACT

With the aim of investigating the solutions of ethane shortage in a commercial ethylene plant, addition of propane as supplementary feedstock and increasing steam to hydrocarbon ratio were proposed as possible strategies. These strategies were proposed to compensate for the ethane shortage in the thermal cracking unit of the commercial plant. Run length, ethylene yield, and propylene yield were considered as the determining factors to appraise the strategies. The major contribution of present work would be the investigation of effect of feed shift on the run length of the steam cracker. Regarding this, five different cases were investigated in real plant condition. To include all the aspects of process, a mathematical model with reasonable assumptions was developed and then validated against the real plant data. Based on the obtained results, increasing propane concentration leads to increase in propylene yield and decrease in ethylene yield. Besides, run length of process was obtained to be longer in the cases with higher propane content in the feed stream.

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1. Introduction

1.1. Olefins

Olefins (also known as alkenes) are aliphatic hydrocarbons with C=C bond. Due to existence of π -type bonds or allylic CH centers leading to unsaturated molecules, olefins tend to participate in a wide range of reactions such as hydration, polymerization, and alkylation [1,2]. Hence, olefins are building blocks for manufacturing various industrial products such as polymers, adhesives, detergents, and solvents. [3–7]. Acyclic mono-olefins with general formula of C_nH_{2n} are commercially produced in petrochemical plants. Thermal cracking, fluid catalytic cracking (FCC), and hydrocracking are the pioneer technologies for converting the heavier hydrocarbons to olefins [3–7]. However, olefins production from waste materials is currently state of the art [8,9]. Ethylene and propylene are of the major utilized mono-olefins in the chemical industries. Growing demand (currently 155 million tons of ethylene per year [6,10]) makes the industries allocate the hydrocarbon sources and investments to ethylene manufacturing. Therefore, ethylene manufacturing is a leading annual mercantile production in the world supplied by pyrolysis of petroleum hydrocarbons.

The type of consumed hydrocarbon to produce ethylene strongly depends on the abundance [6,7]. Utilizing ethane leads

to higher efficiency and selectivity of ethylene compared to the heavier feedstocks. Besides, the processing is comparatively simple and includes lower capital costs [11]. Hence, the obtained ethane from natural gas is the foremost feedstocks for ethylene manufacturing. Production of minimum propylene is the characteristic of ethane thermal cracking furnaces [6,7]. Recently, the demand for propylene has shown more increase comparing ethylene. Hence, proposing new strategies for simultaneous ethylene and propylene production by utilizing the available feedstocks and facilities is currently of a great interest [7]. In addition to this, feeding the cracking reactors with the mixed streams of ethane and propane could probably lead to elimination or even reduction of upstream separation costs [12,13].

1.2. Thermal cracking

Thermal cracking was primarily developed for refinery processing in the early 1920s with the focus on enhancing the quantity and quality of gasoline components. The major portion of low molecular weight olefins, *i.e.* ethylene, propylene, and butylene, is produced as the by-product of this process. Catalytic cracking is another route to manufacture propylene and butylene. However, this process suffers from low ethylene yield [6,7]. In a general point of view, thermal and catalytic cracking are the most conventional routes to convert the gaseous (e.g. ethane, propane, and butane) or liquid (e.g. liquefied petroleum gas (LPG), naphtha, gas oil, and vacuum gas oils) hydrocarbons to ethylene and propylene.

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Nomenclature

A	pre-exponential factor
A_c	cross section area (m^2)
C_{pj}	heat capacity of component j (J/mole/K)
d_t	coil diameter (m)
D_1	inner diameter of coil (m)
D_2	outer diameter of coil (m)
E	activation energy (J/mole)
F_j	molar flow rate of component i (mole/s)
F_r	friction factor
G	total mass flow rate ($kg/m^2/s$)
h_i, h_o	convection coefficient ($W/m^2 K$)
k_i	rate coefficient of reaction i
k_c	thermal conductivity of coke ($W/m/K$)
k_w	thermal conductivity of coil wall ($W/m/K$)
M_m	average molecular weight (kg/kmol)
NC	number of components
NR	number of chemical reactions
P_t	total pressure (pa)
Q	heat flux (W/m^2)
R	universal gas constant (J/mole/k)
R_b	radius of tube bend (m)
R_t	total resistance ($m^2 K/W$)
Re	Reynolds number
r_i	rate of reaction i ($mole/m^3/s$)
S_{ij}	stoichiometric coefficient of component jth in reaction ith
T, T_g	process gas temperature (K)
T_f	furnace temperature (K)
T_w	tube wall temperature (K)
t	time (s)
t_c	coke thickness (m)
U	overall heat transfer coefficient ($W/m^2/K$)
u	gas velocity (m/s)
z	axial reactor coordinate (m)

Greek letters

ΔH	heat of reaction (J/Kmole)
α	coking factor
η	conversion factor (atm/pa)
Λ	angle of tube bend (degree)
ξ	tube bend parameter
ρ_c	coke density (kg/m^3)
ρ_g	gas density (kg/m^3)
σ	Boltzmann constant ($W/m^2/K^4$)

1.3. Simultaneous ethylene and propylene production

In the near future, growth in demand for propylene is expected to outpace the one for ethylene. As mentioned previously, propylene is a by-product of ethylene manufacturing, particularly in steam cracking process. Middle East has the capacity of approximately 0.02 tons propylene per ton of ethylene, which makes product imbalance problem in this region [12]. In order to deal with such a problem, task specific technologies for propylene production, such as propane dehydrogenation [16,17], olefin metathesis [18], and FCC [7] processes have been developed recently. In this regard, Akah and Al-Ghrami [19] investigated the enhancement of propylene production in FCC process and expected that the appropriate catalyst, reactor configuration, and reaction condition have the most impact on the propylene yield. In modeling studies, thermal cracking of ethane, propane, and their mixtures was investigated by Sundaram and Froment [20] and Belohlav et al. [21]. In these studies, different kinetic models for thermal cracking of olefins were presented. In a subsequent study, Sundaram and Froment developed radical schemes for pyrolysis of butanes and their mixtures with ethane and propane [22]. A dynamic mathematical model was developed by Shahrokhi and Nejat [23] to obtain optimum temperature profile in the propane thermal cracking reactor. Berreni and Wang [12] developed a mathematical model and a dynamic optimization procedure to determine the optimum condition of propane thermal cracking for ethylene production. Zarinabadi and Samimi [24] presented a mathematical model for olefin production in a commercial petrochemical plant and then investigated the impact of coil outlet temperature on the yields of ethylene and propylene. In another study, Keyvanloo et al. [25] perused the effect of temperature, steam to naphtha ratio, and residence time on the efficiency of light olefins in steam cracking of naphtha [25]. Ethylene production through thermal cracking of naphtha in the presence of steam or carbon dioxide was investigated by Haghghi et al. [26]. Presence of carbon dioxide led to achievements in inhibiting coke formation. In a further study, Yancheshmeh et al. [27] determined the effects of steam and carbon dioxide dilution on the ethylene and hydrogen production in the ethane pyrolysis process.

In a practical work, Sims [28] presented a patent for cracking of ethane and propane mixtures. The process includes a fractionation step for the separation of the feedstock and producing ethane-rich and propane-rich streams, separate furnaces for steam cracking of each stream, ethylene recovery, and residual ethane and propane recycling into the furnaces. Enhanced ethylene yield is the advancement of this process. More recently, Yuan et al. [29] investigated the co-cracking of various hydrocarbon mixtures of ethane, propane, LPG, and naphtha in a steam pyrolysis furnace by using software packages of COILSIM1D and SimCO. The effects of various operating variables such as feed composition, coil outlet temperature, and pressure were investigated. Lower profitability of co-cracking of ethane/propane mixtures comparing the cracking of pure feedstocks were reported in their study. Model validation was carried out by comparing the results of software packages with the real data of naphtha and LPG cracking. However, real plant data of ethane and propane co-cracking in real plant condition were not utilized to validate the model for this type of feedstock. Besides, the effect of operating variables on the coking phenomena and the run length of cracking furnace was not investigated.

The effect of utilizing one-dimensional or two-dimensional mathematical models on the product yield of cracking reactor was investigated by Van Geem et al. [30]. They showed that by applying a two-dimensional model less ethylene yield is calculated. Moreover, the impact of the radial gradients on the rate of coke formation was determined. They concluded that two-dimensional model is more accurate in the prediction of coke formation rate.

However, the major part of ethylene and propylene is still produced by thermal cracking. In the current status, 95% of global ethylene production capacity is obtained by utilizing thermal cracking. Besides, 60% of global propylene capacity is produced by this process [7]. More details of cracking processes could be found in the recent reviews of Sadrameli [6,7].

Utilizing steam in the cracking process provides the high temperature condition in the furnaces and improves the yield of process. In fact, blending the preheated hydrocarbon feed with the steam results in increasing feed temperature, diluting the heavy hydrocarbon feed, and reduction of coke formation and thus pressure drop along the reactor. Depending on the feedstock type, the desirable steam to hydrocarbon ratio varies in the range of 0.2–1.0. Lower steam to hydrocarbon ratio is favorable in the case of lighter hydrocarbon feedstock such as ethane and propane [6,14]. Increasing steam to hydrocarbon ratio increases the temperature and thermal energy of feed stream [6,15].

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