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Review article

Thermal/catalytic cracking of liquid hydrocarbons for the production of olefins: A state-of-the-art review II: Catalytic cracking review

S.M. Sadrameli

Chemical Engineering Department, Tarbiat Modares University, P.O. Box 14115-114, Tehran, Iran

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ABSTRACT

Light olefins such as ethylene and propylene, are considered as main raw materials for the production of numerous plastic materials, synthesis fibers and rubbers in the petrochemical industry. The conventional process for the production of light olefins is thermal cracking in the presence of steam called Steam Cracking (SC). This has been the main technology for the production of olefins for more than ninety years. This technology has reached to its full capacity and cannot accommodate excessive demands of the petrochemical industry although still 95% of the light olefins are produced by this technology. In addition there are a few drawbacks for this technology such as en extensive energy consumption, and production of greenhouse gasses. An alternative and promising route for the production of light olefins which consumes less energy and produces fewer pollutants to the environment is Thermal Catalytic Cracking (TCC). This paper reviews the main research works done on the process in the literature in the last five decades. An eight-lump mathematical model is presented for the catalytic cracking kinetics. Some of the main experimental laboratory setup systems in the world have also been reviewed and parts of the results are presented and discussed.

Contents

1. Introduction

Olefins which are in the class of unsaturated hydrocarbons with a single double bond and a chemical formula of C_nH_{2n} are one of the most important chemicals and raw materials in the petrochemical industry. The commercial production of ethylene has been first patented by Union Carbide in 1922 [1] and three years later the first commercial plant for ethylene production was built in Virginia in the United States. Since then the plants for the production of olefins have been bigger, more efficient in energy consumption,

E-mail address: sadramel@modares.ac.ir

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Nomenclature

C/H	atomic ratio of carbon to hydrogen in feeds	t	residence time, s
C_i	concentration of lump i, mol/g_{gas}	t_c	residence time of catalyst, s
E	activation energy, kJ/mol	T	reaction temperature, K
k_{ij}	rate constant for the reaction of lump i to lump j	υ_{ij}	stoichiometric coefficient for the reaction of lump I to lump j
M_i	molecular weight of lump i, g/mol		
R_{co}	catalyst to oil weight ratio	*Greek letters*	
R_{so}	steam to oil weight ratio	α	deactivation constant
		ϕ	deactivation function

and more environmentally friendly. The plant capacity for today's world scale crackers is more than 1.5 million MTY. The conventional technologies for the production of light olefins are Steam Cracking (SC), Fluidized Catalytic Cracking (FCC) using zeolites, Deep Catalytic Cracking (DCC), and Methanol to Olefins (MTO). Worldwide olefin's demand is primarily driven by economic growth and the associated increased demand for consumer goods. The demand for ethylene is increasing and the present demand by petrochemical industry is over 155 million tons per annum [2,3].

Ethylene producers in the world are looking for the more accessible lower price feeds for the production of olefins. Ethane separated from natural gas and natural gas liquids is one of the more available feeds for the cracking in the world and therefore most of the cracking furnaces utilize this feed for the production of light olefins. The ethane crackers produces the minimum amounts of propylene and the recovery of this product is not feasible in such industrial plants. Normally for each tone of ethylene production, 0.4 tone of propylene is produced in the thermal cracking furnace. It is expected that by growing ethane cracking furnaces by 2014 the ratio of propylene to ethylene reaches to the lowest value of 0.36 while this ratio by the petrochemical demands is 0.62 [2]. Nearly 68% of the world propylene is produced besides ethylene by thermal cracking process, 29% by FCC process with catalytic cracking in the refineries, and 3% produced with other process [4]. The steam cracking furnaces produce propylene as a byproduct when using feeds other than ethane which is always less than ethylene. The propylene market grew more than ethylene and the demand for the propylene exceeded the demand for ethylene in recent years as illustrated in Fig. 1 [5]. Therefore, there is a need for the new technologies that can fill the market gap for the production of propylene using the commonly available feeds. This can be achieved by using thermal catalytic cracking with more selectivity to the propylene production. The thermal catalytic

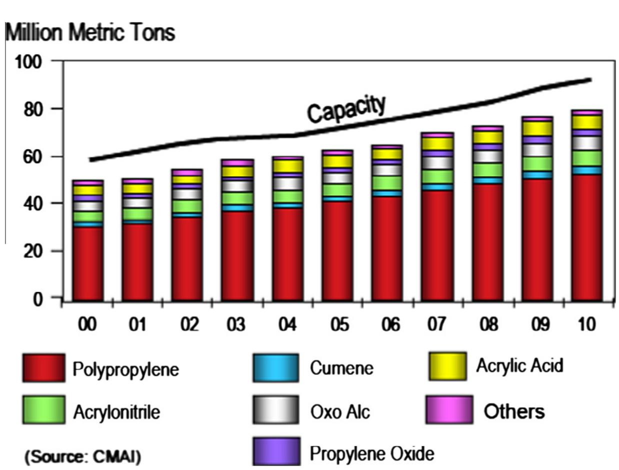

Fig. 1. Propylene demand growth [5].

cracking process is performed in different types of reactors such as a fixed-bed or a fluidized bed reactor at moderate temperature in the presence of catalyst. The main objective of the process is cracking of low value hydrocarbons for the production of higher valued products. The catalyst can increase the selectivity of the process at lower temperature than in the thermal cracking for the production of light hydrocarbons.

In the first part of this review paper [6] the thermal cracking of gaseous and liquid hydrocarbon feeds for the production of light olefins has been discussed. This paper reviews the thermal catalytic cracking of liquid hydrocarbons for the production light olefins. Some of the experimental research works done in the last decades on the catalytic cracking of liquid hydrocarbons for the production of light olefins using different types of catalysts are reviewed and parts of the results are presented. A kinetic mathematical model for the simulation of the fixed bed reactors is presented and finally some of the main experimental setup systems in the world in which the catalytic cracking for the production of light olefins are studied are discussed.

2. Catalytic cracking

Thermal cracking or steam cracking is still the main route for the production of light olefins and currently produce 95% of the world's ethylene and 60% of the world's propylene as a byproduct to ethylene production [7]. A schematic diagram of a steam cracker including the furnace, an indirect quench system called transfer line exchange (TLE or TLX), and direct quench system using quench oil is shown in Fig. 2. The main production of propylene from steam cracking is mainly from LPG and heavier liquid feeds such as naphtha and gas oil; and even then this is limited to about half that of ethylene typically with the weight ratio approximately 0.4–0.6 parts of propylene to ethylene [8]. This would not satisfy the world's demand for propylene by petrochemical industry and therefore the new sources of propylene will be necessary to satisfy the expected industrial demand in the future. Thermal cracking furnaces are also one of the most energy-intensive processes that typically operate at 850–900 °C and produce a large amount of greenhouse emissions. Pyrolysis section alone utilizes 65% of the total energy use and 75% of the total exergy loss in the plant. Such furnaces also require being out of service for decoking as a result of high process temperature [8]. One of the solutions to address all of these drawbacks will be the application of new technologies for the olefin production. Liquid and wasted solid hydrocarbons such as polymers can be cracked by thermal catalytic cracking to produce large amount of ethylene and propylene.

2.1. Previous research works on TCC

2.1.1. Oxides catalysts

Thermal catalytic cracking has been investigated experimentally by Mjukhopadhyay and Kunzru [9] using modified alumina