

# Application of response surface methodology for optimization of an industrial methylacetylene and propadiene hydrogenation reactor



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## ABSTRACT

This paper presents the application of a statistical model in the optimization of an industrial methylacetylene-propadiene (MAPD) hydrogenation reactor of domestic olefin plant. The effects of fresh feed flow rate, MAPD inlet concentration, the amount of diluent and hydrogen flow rates on the propylene gain were investigated using response surface methodology (RSM) by Minitab software. According to Multilevel factorial design a total of 192 experiments were carried out. To identify the significance of the effects and their interactions, analysis of variance (ANOVA) was performed for each parameter on the outlet concentrations of propylene, MAPD and propane. The results indicate that the  $R^2$  values are more than 0.95 and adjusted  $R^2$  are in a reasonable agreement with  $R^2$ . According to the optimal conditions, the maximum amount of propylene production, as the main goal of this study is gained in the lowest value of MAPD inlet concentration (2 mol%) and hydrogen flow rate and in the high values of fresh feed and diluent flow rates.

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## 1. Introduction

Steam cracking is a process that takes place at high temperatures for converting heavy hydrocarbons to light hydrocarbons in the presence of steam [1]. Hydrocarbon feed, including naphtha, liquefied petroleum gas (LPG) and ethane, decomposes into hydrogen, methane, and olefins such as ethylene and propylene [2]. Propylene ( $C_3$ -cut), as an important building block in the chemical industry is used to make two widely applied polymers (polypropylene and polyurethane) as well as a range of chemical intermediates [3]. The  $C_3$ -cut obtained by the steam cracking of hydrocarbons, as the major source of propylene production, typically contains more than 90% propylene and up to 6% methyl acetylene (MA) and propadiene (PD) which are poisonous to catalyst for propylene polymerization and would

severely reduce the quality of polypropylene [2]. The methyl acetylene-propadiene (MAPD) content in  $C_3$ -cut stream depends on the type of feed and on the stiffness of the steam cracking [3]. A MAPD converter is usually required to improve the yield as well as purity of the propylene stream [4]. For this reason, refining by catalytic selective hydrogenation has an important role because it has two advantages: it reduces or completely eliminates the content of the highly unsaturated compounds, and reduces olefin losses in the secondary reactions. Nevertheless, hydrogenation has to be very selective in order to avoid the risk of losing olefins by reaction with hydrogen to paraffins. Selectivity is possible by using catalysts [1]. Both gas phase and liquid phase selective hydrogenation of MAPD are in use in industry [3]. The gas-phase selective hydrogenation process was performed well in the early naphtha cracker process, but the use of the liquid phase selective hydrogenation process has gradually increased instead in current petrochemical processing plants [4]. It is accepted that the liquid phase operation offers some advantages over the gas phase process in operating cost and catalyst life, due to the removal of produced oligomers from the catalyst surface by the liquid flow [3]. Among the three-phase gas-liquid-solid reaction systems in the chemical industry, trickle-bed reactors (TBRs) are widely used for various hydrogenation reactions because of their flexibility and simplicity

**Abbreviations:** BFW, boiler feed water; LHHW, Langmuir–Hinshelwood/Hougen–Watson; LP, low pressure; LPG, liquefied petroleum gas; MA, methylacetylene; MAPD, methylacetylene-propadiene; PD, propadiene; TBR, trickle-bed reactor.

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### Nomenclature

$D$	diluent molar flow rate
$F$	fresh feed molar flow rate
$MW$	molecular weight
$R$	reactor feed molar feed flow rate
$x_i$	mole fraction of stream $i$

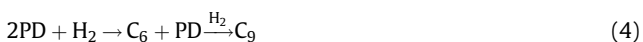
in operation for low as well as high throughputs. Most commercial TBRs normally operate adiabatically. Operating at elevated temperatures and pressures, they succeed in attaining high conversion per catalyst mass with minimum power consumption that makes them favorable to chemical engineers. In trickle bed reactors gas and liquid phases flow co-currently downward through a fixed bed of catalyst particles [5–8].

To obtain high purity propylene for polymerization, Pd/Al<sub>2</sub>O<sub>3</sub> catalyst is commonly used in the industrial process for converting MAPD selectively to propylene [9]. Palladium is the most active and selective metal for the hydrogenation of alkynes to the corresponding olefins. Presently, all industrial catalysts used in selective hydrogenation are bimetallic catalysts with a palladium active phase supported on alumina and promoted by another metal. In the hydrogenation process over Pd/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, two kinds of active sites, *i.e.*, metal sites and acid sites, are involved. The metal sites catalyze hydrogenation reactions, but the acidity of the alumina catalyzes oligomerization of the olefins, thus producing the so-called green oil [3]. The selective hydrogenation reactions including the propylene formation reaction and the formation of oligomers (green oil) are shown as follows. In the propylene formation reaction, MA and PD are hydrogenated over Pd active sites to form propylene, which is subsequently hydrogenated to form propane [4].

(i) The propylene formation reactions:



(ii) The oligomer formation reactions:



The kinetic analysis of selective hydrogenation of MAPD has been a topic of considerable researches over the past several decades. Most of the work was addressed via the experimental setup and some of them have been investigated in some kinds of industrial reactors.

A kinetic study of the selective hydrogenation of a C<sub>2</sub>–C<sub>7</sub> mixture over two palladium/alumina catalysts with front-end variant was presented by Godinez et al. [9]. Fajardo et al. [1] studied the gas phase kinetics of hydrogenation of MAPD in a plug-flow reactor over a commercial palladium-based catalyst. The influence of feed composition, temperature and hydrogen/hydrocarbon ratio of the feedstock on the fractional conversion was studied and acceptable models describing the kinetics of MAPD hydrogenation were derived. The kinetics of MA and PD hydrogenation reactions in liquid phase was searched by Uygur et al. [10] in 1998. Rate equations for MA, PD were described by a reaction mechanism derived according to LHHW model. It was found that MAPD conversion to propylene decreases as temperature and WHSV increases. Wang and Froment [3] developed a

kinetic model for the gas phase selective hydrogenation of the C<sub>3</sub>-cut of a thermal cracking unit. In addition to the hydrogenation reactions on metal sites, the green oil formation on acid sites and the catalyst deactivation were also considered in the proposed kinetic model. Finally, the kinetic model was plugged into the reactor model to simulate an industrial adiabatic reactor. Wu et al. [4] identified the kinetics of MA and PD selective hydrogenation by nonlinear regression technique. The effect of catalyst deactivation by green oil was investigated through the dynamic modeling of non-isothermal hydrogenation reactor. It was found that in addition to the high MAPD conversion and low operating temperature, the desired operating manner depends on the propylene selectivity. In another related work, the optimization and simulation of the industrial selective hydrogenation process composed of two hydrogenation reactors is addressed by Wu and Li [11]. The simulation results showed that the desired operating condition was determined regarding to the ratios of H<sub>2</sub> to MAPD at each reactor and the recycle ratio.

Optimal production of propylene has been considered as one of the most important operational concerns since the start of Jam Petrochemical Company. Due to the variety of liquid feedstock and the dual nature (composition of the gas and liquid feed) of cracking section in Jam olefin unit, the control of the optimal operating parameters of MAPD hydrogenation reactor has been always as one of the main issues. The control of the amount of MAPD in the propylene production tower and the selectivity of propylene is very important. In the current work, response surface methodology (RSM) by Minitab software was used to determine the optimal response of propylene production rate to various parameters such as fresh feed, diluent and hydrogen flow rates as well as MAPD concentration at the inlet of an industrial MAPD hydrogenation reactor. A total of 192 experiments were considered according to multilevel factorial design. Therefore, to identify the significance of the effects and the interactions between them, analysis of variance (ANOVA) was done for each parameter.

## 2. Process description

### 2.1. General plant

Olefin Unit of Jam Petrochemical Complex as Tenth National Petrochemical Company is currently one of the world's largest producers of ethylene and propylene (it was designed for the annual production of about 1,300,000 and 320,000 ton of ethylene and propylene, respectively). As clears, propylene is the second most important product of the olefin unit and due to its high value, the careful and regular production of that seems to be very critical.

A block diagram of this unit is depicted in Fig. 1. The feedstock of the olefin unit is prepared through several pipelines and include liquid feed (raffinate, C<sub>5</sub> cut, light ends, C<sub>5</sub><sup>+</sup> and LPG), ethane and C<sub>3</sub><sup>+</sup> cut stream. The olefin unit consists of series of furnaces that are known as the pyrolysis furnaces. The furnace section, as the heart of the ethylene plant, converts raw feedstock to products, while the downstream sections are concerned with separation and purification of these products. The cracking can be done both in the vapor and liquid phase. Liquid and gaseous feedstock will be cracked separately each in dedicated furnaces.

Fig. 2 gives a schematic view of a typical olefin plant. The recovery of ethylene and heavier components from the cracked gas is achieved by condensation in the cold train and by De-Methanization of the condensates. The streams from the De-Methanization section feed separately the De-Ethanizer tower. The hydrogenation is performed in the adiabatic reactors selected for both ease of operation and investment reasons. The C<sub>3</sub> cut fractionation is achieved in the De-Propanizer tower. This column receives feeds from the De-Ethanizer bottom product. The C<sub>3</sub> cut

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