Optimization of Naphtha Steam Cracking Conditions for Production of Light Olefins by Statistical Design of Experiments

pezhman sandiani1

1Department of Chemical Engineering, Sharif University, Tehran, Iran

Abstract

The effect of temperature, steam to naphtha ratio, and residence time on the yield of the major products in naphtha steam cracking has been investigated. The temperature, steam ratio, and residence time were varied in the range 1053-1153 K, 0.5-0.9 gr/gr, and 0.15-0.4s, respectively. Based on experimental results, naphtha steam cracking was modeled by use of statistical design of experiments. Good agreement was obtained between the calculated and experimental results. The results for the successful multi-objective optimization of the naphtha steam cracking have also been reported. Performance was assessed using two quantitative descriptors: yields of ethylene and propylene. The response defined by the three most significant parameters was obtained from Box-Behnken design and the optimal parameter set was found. The superiority of the DoE method over the conventional COST (change one separate factor at a time) approach is shown by the fact that we were able to optimize three individual factors with only 13 runs.

Keywords: Naphtha steam cracking, Ethylene and propylene yield, Optimization, Statistical design

1 Tel: +989192470264
Email address: peji.sandiani@gmail.com

1. Introduction

Ethylene and propylene are the two most important light olefins. They are important reaction intermediates in industrial organic synthesis and being staple feedstocks in petrochemical industry. They used in production of plastics, fibers, lubricants, etc. Their production process, steam cracking, has the backbone status for the sector. Hydrocarbon feed mixed with process steam is introduced into the tubular reactors (cracking coils) with short residence time and at a high temperature. Steam is used to increase the olefin selectivity and to reduce the coke formation by decreasing the hydrocarbon partial pressure. The product yields depend on various factors, such as residence time, temperature, and average hydrocarbon partial pressure. Several investigators have studied the kinetics and product yields during pyrolysis of naphtha [1-4]. The usual experimental strategy for synthesis optimization is the COST (change one separate factor at a time) approach: all variable but one are fixed at predetermined values, and the response of the system is studied as a function of the changing variable. Each variable is scanned this way, and the combination of their optimum values is accepted as the global optimum. The two major shortcomings of this approach are (i) the amount of necessary experiments grows very fast with the number of variables, thus, the complete optimization of real systems is rather unfeasible, and (ii) it is very unlikely that the global optimum can be found this way. The
reason for this is that COST assumes that the effects of the variables are completely independent, whereas the
response of a real system to a change in any single parameter appears often as the gross effect of several
parameter alternations (that is, real life multi-dimensional parameter spaces are seldom orthogonal) [5].
Statistical design of experiments (DoE) is the science of obtaining the largest possible amount of information
about a system with small number of experiments [6]. Albeit DoE is rapidly gaining popularity in various fields
related to material science [7,8] and catalysis [9], it’s a new approach for naphtha steam cracking that has been
reported.
In the present model study we prove that the DoE approach can be utilized successfully for the rapid
optimization of naphtha steam cracking. We study the key factors affecting steam cracking yield and fit the
response surface using a Box-Behnken design. The goal of the optimization is to achieve the best compromise
between ethylene yield and propylene yield.

2. Experimental set-up

Experiments were performed using a one zone tubular furnace. The reactor vessel consisted of a stainless steel
tube 45 cm in length and 1.345 cm in diameter. Liquids, naphtha and water, were injected into a vaporizer using
two pumps. Steam, which was used as an inert, was generated in a vaporizer and mixed with the naphtha before
the preheater. To avoid cracking in the preheat section the temperature of the preheated mixture was kept below
550°C and this mixture was then fed to the reactor. The effluent from the reactor was quenched in ice bath
followed by two water-cooled condensers placed in series. The gas-phase components were analyzed using a
Hewlett-Packard 5890 Flame Ionization Detector (FID) gas chromatograph (GC) equipped with Agilent J&W
GS-alumina column (30 m × 0.53 mm × 30 µm). The steam cracking results reproducible within ± 2.0 wt. %.

3. Results and discussion

3.1. Initial screening of the parameter space

Efficient optimization requires the early identification of key process parameters. Based on our previous
experience with steam cracking we included the following process variables in the optimization: (i) temperature,
(ii) steam/naphtha and (iii) residence time. They were varied in the range 780-880°C, 0.5-0.9 gr/gr, and 0.15-
0.4s, respectively.

3.2. Response surface exploration

The next step of the optimization was to collect enough data so that the response surfaces defined by the three
chosen variables could be fitted. The least resource-demanding design which is able to identify non-linear
relationships for the three factors is the three-level Box-Behnken design with one center point. This is an
independent quadratic design in which parameter combinations are at the center and at the midpoints of edges of
the process space. Some advantages of the Box-Behnken design over other responses surface optimization
schemes (e.g., central composite designs, three-level full factorial designs etc.) are (i) it requires the smallest
number of runs for three factors at three levels, (ii) it ensures that the process remains always within the safe
operation zone and (iii) it ensures that all factors are not set at their highest levels simultaneously. Our composition required 13 runs. These results are shown in Table 1. Each run was analyzed for ethylene and propylene yield. It can be seen from the contour plots presented in Figure 1 that each of the three optimized variables affects both measured responses.

**Table 1.** Ethylene and propylene yields for Box-Behnken design

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature (°C)</th>
<th>Residence time (s)</th>
<th>Steam ratio (gr/gr)</th>
<th>Ethylene (wt%)</th>
<th>Propylene (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>780</td>
<td>0.4</td>
<td>0.7</td>
<td>31.87</td>
<td>21.31</td>
</tr>
<tr>
<td>2</td>
<td>880</td>
<td>0.28</td>
<td>0.5</td>
<td>33.08</td>
<td>14.28</td>
</tr>
<tr>
<td>3</td>
<td>780</td>
<td>0.15</td>
<td>0.7</td>
<td>19.15</td>
<td>14.33</td>
</tr>
<tr>
<td>4</td>
<td>830</td>
<td>0.15</td>
<td>0.9</td>
<td>25.74</td>
<td>17.47</td>
</tr>
<tr>
<td>5</td>
<td>880</td>
<td>0.15</td>
<td>0.7</td>
<td>32.39</td>
<td>17.82</td>
</tr>
<tr>
<td>6</td>
<td>830</td>
<td>0.4</td>
<td>0.5</td>
<td>36.24</td>
<td>15.76</td>
</tr>
<tr>
<td>7</td>
<td>830</td>
<td>0.28</td>
<td>0.7</td>
<td>32.09</td>
<td>19.66</td>
</tr>
<tr>
<td>8</td>
<td>880</td>
<td>0.28</td>
<td>0.9</td>
<td>35.41</td>
<td>14.82</td>
</tr>
<tr>
<td>9</td>
<td>880</td>
<td>0.4</td>
<td>0.7</td>
<td>39.27</td>
<td>6.20</td>
</tr>
<tr>
<td>10</td>
<td>830</td>
<td>0.15</td>
<td>0.5</td>
<td>21.37</td>
<td>16.76</td>
</tr>
<tr>
<td>11</td>
<td>830</td>
<td>0.4</td>
<td>0.9</td>
<td>40.012</td>
<td>14.94</td>
</tr>
<tr>
<td>12</td>
<td>780</td>
<td>0.28</td>
<td>0.9</td>
<td>27.66</td>
<td>20.45</td>
</tr>
<tr>
<td>13</td>
<td>780</td>
<td>0.28</td>
<td>0.5</td>
<td>18.25</td>
<td>15.37</td>
</tr>
</tbody>
</table>

Therefore the results were fitted using full quadratic response surface equations given in Eqs. (1) and (2):

\[
Ethylene = -759.6912 + 1.5114a + 232.3752b + 219.072c - 0.2336ab - 0.177ac - 5.98bc + 26.256b^2 - 41.4937c^2
\]  
\[
Propylene = -860.8441 + 1.817a + 703.6688b + 138.965c - 0.744ab - 0.1135ac - 15.3bc - 152.015b^2 - 26.5062c^2
\]

where a, b and c denote "temperature", "residence time", and "steam ratio", respectively.
Fig. 1. Contour plots describing the response surface for both (a), (b), and (c) ethylene yield and (e), (f), and (g) propylene yield as a function of each parameter pair. The third parameter in each figure is kept fixed at midpoint.

The equation developed was used to compare the experimental and predicted yields at our mentioned process conditions. Figure 2 and 3 show the comparison between the experimental and calculated yields of ethylene and propylene.

Fig. 2. Predicted vs. experimental for ethylene yield.
The variables that affect the cracking reactor performance and were discussed in our experimental design were chosen as the decision variables. The ranges of decision variables used are as follows:

\[
800 \, ^\circ \text{C} \leq T \leq 850 \, ^\circ \text{C} \\
0.15 \, \text{s} \leq \text{residence time} \leq 0.3 \, \text{s} \\
0.5 \, \text{gr/g} \leq \text{steam ratio} \leq 0.7 \, \text{gr/g}
\]

Bounds on the decision variables are selected according to industrial practice. The results of multiobjective optimization can be used to recommend the operating conditions for further experimental works in naphtha steam cracking especially in the kinetic studies.

A parameter set which is able to maximize either ethylene and propylene yield could be obtained analytically from Eqs. (1) or (2). However, our goal is to optimize the light olefins (ethylene and propylene) and this requires the simultaneous maximization of both responses. On the other hand, by minimization of steam ratio we can approach to industrial process condition. The scaled value was denoted as the “desirability” (D) of a certain parameter set with respect to the studied response, and the composite desirability \(D_{\text{comp}}\) of a parameter set was defined as the linear combination of the individual \(d\) values, as shown in Eq. 3. This is a general approach to cut the dimensionality of a simultaneous optimization problem to just one: finding the parameter set which maximizes \(D_{\text{comp}}\).

\[
D_{\text{composite}} = \left( \prod_{i=1}^{n} d_i \right)^{\frac{1}{n}}
\]

In our case the optimum was found at temperature = 836.06°C, residence time = 0.3s, steam ratio = 0.7gr/gr. This set gave the highest \(D_{\text{comp}}\) at 0.779 and predicted ethylene yield=33.92 wt% and propylene yield=18.94 wt% for optimized responses.

As we have expected, the values of residence time and steam ratio are at their upper limit. Due to the fact that increasing the steam ratio decreases partial pressure and the rate of coking; thus the yield of ethylene and propylene is increased simultaneously. Temperature has an opposing effect on yield of ethylene and propylene; high temperature maximizes ethylene production while low temperature maximizes propylene production. As we can see, the maximum yield of combined ethylene and propylene is occurred at an intermediate temperature.

4. Conclusion

We reported on the successful application of the statistical design of experiments approach for the optimization of naphtha steam cracking. Based on our previous experience with steam cracking we identify the three factors affecting performance, which were then optimized using Box-Behnken design. Thus, in 13 runs we were able to
achieve the best performance on our local experimental bench. Temperature is the most important decision variable and has an opposing effect on the yield of ethylene and propylene. The influence of other decision variables such as residence time and steam ratio, also considered.

References