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Characterising carbon deposited during pyrolysis gasoline hydrogenation: enhanced TPO methodologies

Javed Ali · S. David Jackson

Abstract In this paper, the use of temperature-programmed oxidation (TPO) is highlighted as a means of interrogating the surface of catalysts. Most studies only concern themselves with the active portion of the catalyst bed; in this study, we examine both the active part and the part that experiences equilibrated gas after reaction. The extent and nature of carbonaceous deposits on both sections of catalyst have been characterised by TPO and reveal that there is significant deposition of low H:C ratio carbonaceous species on catalyst that has only seen equilibrated reaction gas. This has potential implications for the life of the catalyst bed and the activity and selectivity observed.

Keywords PyGas · Hydrogenation · Temperature programmed oxidation · Carbon deposition

Introduction

Pyrolysis gasoline (PyGas) is a by-product of high temperature naphtha cracking during ethylene and propylene production [1, 2]. It is a mixture of highly unsaturated hydrocarbons ranging from C_5 to C_{12} and contains considerable amounts of aromatics, typically 40–80 % (benzene, toluene and xylene), together with paraffins, olefins and diolefins [3]. Composition of the PyGas produced depends on the feedstock and operating conditions and varies from plant to plant; however, a typical PyGas composition is given in Table 1 [8].
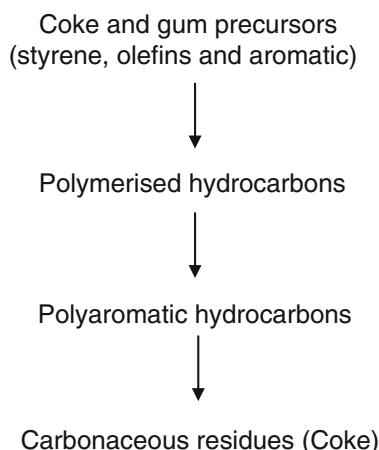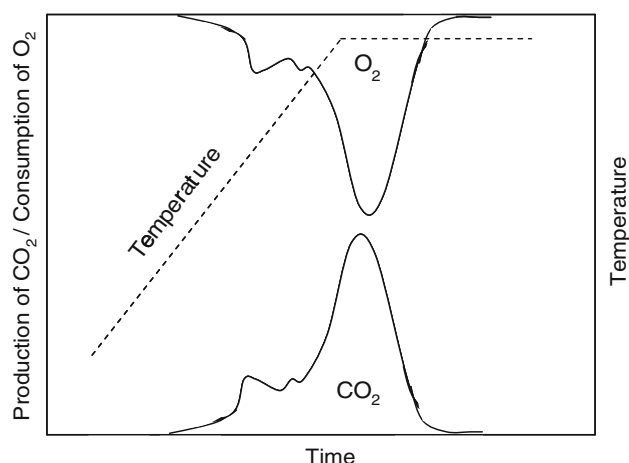
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The main reason for the deactivation of catalysts during PyGas hydrogenation is the deposition of carbonaceous residue (coke) on the surface of the catalyst [10, 11]. The nature of the coke depends on the process conditions and length of reaction with the carbonaceous residues deposited, varying from hydrocarbons and poly-aromatics to graphitic coke. The deposition of coke decreases accessibility for the reactants to the catalyst surface and can block pores. Continued heavy build up of coke in pores may result in fracturing of the support material which can cause plugging of reactor voids [7, 13].

Carbonaceous residue formation is mainly due to the polymerisation of coke precursors present in PyGas such as styrene, di-olefins, mono-olefins, cyclo-olefins and aromatic species [14]. The deposited residue can convert to polyaromatic hydrocarbons, which then further convert to highly condensed polyaromatics and graphitic type coke. This is summarised in Fig. 1 [7, 9].

The nature of the carbonaceous residues also changes with reaction time. The change in the nature of the coke is due to polymerisation, multi-side reactions and loss of hydrogen content. The deposits convert to more condensed and hydrogen deficient coke with the passage of time and then finally form graphitic type coke.

The deposition of coke is highly dependent on the reaction conditions, especially on reaction temperature and hydrogen partial pressure. Increases in the reaction temperature of PyGas hydrogenation not only increase the amount of coke deposition but also result in a more condensed hydrogen deficient coke on the surface. Carbon laydown can be decreased by increasing hydrogen partial pressure [1].

Temperature-programmed oxidation (TPO) is a simple and important technique for the investigation into the quantity and nature of coke deposited [5, 6]. The amount of

Table 1 Typical composition of PyGas

PyGas components	Weight percent (wt%)
Benzene, toluene and xylenes	50
Olefins and dienes	25
Styrene and other aromatics	15
Paraffins and naphthenes	10

Table 2 Catalyst specifications

Catalyst	Metal loading (%wt)	Metal dispersion (%)	Surface area $(m^2\ g^{-1})$	Pore volume $(cm^3\ g^{-1})$
Ni/Al_2O_3	16.0	18.0	106	0.39

to carbon ratio represents more condensed polyaromatic type of coke [6].

In this paper, we use TPO to probe the carbon deposit in both the reaction zone and the rest of the catalyst bed that is subjected to equilibrated gas in the typical fixed bed configuration found in the most chemical plants.

Coke and gum precursors
(styrene, olefins and aromatic)

↓

Polymerised hydrocarbons

↓

Polyaromatic hydrocarbons

↓

Carbonaceous residues (Coke)

Fig. 1 Formation of carbonaceous residues (Coke)

Fig. 2 Typical temperature programme oxidation profile [5, 6]

Experimental

The Ni/Al_2O_3 (HTC 400) catalyst used in this project was provided by Johnson Matthey. The characterisation data of catalyst provided by catalyst manufacturer are shown in Table 2.

Hydrogenation of the synthetic pyrolysis gasoline (PyGas) was investigated over the Ni/Al_2O_3 catalyst in a fixed-bed, high-pressure, continuous flow reactor. The catalyst (particle size between 250 and 425 microns) was added to the reactor tube and positioned in the middle of reactor tube. The catalyst was reduced in situ with a flow of hydrogen gas. The Ni/Al_2O_3 catalyst was reduced for 16 h at a temperature of 723 K. Following this, the reactor temperature was decreased to the required reaction temperature (413 K). The reactor was then pressurised to the desired pressure (20 barg). Once the reactor had obtained the desired conditions, the reaction was started with a particular flow of PyGas feed of 0.042 ml min^{-1} (WHSV$_{PyGas}$ 8 h^{-1}) and a flow of H_2/N_2 gas (10 ml min^{-1}). The PyGas was vaporised and mixed with hydrogen and then passed through the catalyst bed. The hydrogenated PyGas was condensed in a knockout pot, which was chilled to 273 K. Liquid samples were collected every 2 h during daytime and analysed using a Thermo Finnigan Focus G.C. The hydrogenated PyGas mainly condensed in the knockout pot; however, very small amounts of the reaction products remained in the gaseous phase and, therefore, the effluent gas was also analysed at regular intervals by online Agilent G.C. All reactions were run for 76 h. After finishing each reaction, nitrogen gas was passed through the catalyst over night so as to remove any species present in the reactor. The reactor was then cooled to room temperature in the flow of nitrogen gas and then an in situ TPO was performed on the post reaction catalyst. The gas was switched to a flow of 2 % O_2/Ar (40 ml min^{-1}) and the temperature increased to 723 K at a ramp of 5 K min^{-1} and then the reactor temperature was held constant at 723 K until all evolution of gases other

oxygen consumed and the amount of CO_2/CO produced indicate the amount of coke deposited on the surface of the catalyst. The oxygen consumption is commonly mirrored by the production of CO_2, as shown in Fig. 2.

The combustion of hydrogen rich coke, which is mostly present on the catalytic metal, occurs first. This is followed by the combustion of the hydrogen deficient coke present on the surface of the catalyst [4, 12]. The ratio of CO_2/H_2O and/or CO/H_2O can give insight into the carbon to hydrogen ratio present in the coke. A decrease in hydrogen

Table 3 Weight percent (%) composition of PyGas

Components	1-pentene	Cyclopentene	1-octene	Toluene	Styrene	Heptane	Decane
PyGas wt%	10.0	10.0	10.0	55.0	10.0	2.5	2.5

than O_2 and Ar ceased. The TPO process was monitored by an online mass spectrometer (QMS) in which the ion current of main species of mass fragments with m/z 28 (CO), 44 (CO_2), 32 (O_2), 18 (H_2O) was monitored. Other species with m/z 68 (cyclopentene), 70 (1-pentene), 72 (pentane), 78 (benzene), 92 (toluene), 98 (methylcyclohexane), 104 (styrene), 106 (ethylcyclo-hexane), 112 (1-octene), 114 (octane), 15 (CH_3), 29 (C_2H_5) and 2 (H_2) were also followed for detailed investigation of deposited coke.

A synthetic PyGas was used in this study and the composition is shown in Table 3. No benzene was used in this mix due to health and safety concerns: toluene was used as a replacement. Heptane and decane were used as internal standards for GC analysis.

Results and discussion

During the course of the time on stream (TOS), the catalyst deactivated. A typical deactivation profile is shown in Fig. 3 with the hydrogenation of toluene to methylcyclohexane. There is a rapid deactivation over the first 24 h followed by a period of much slower deactivation. This behaviour was observed with all reactants. At the end of the 76-h TOS, the catalyst was subjected to an in situ TPO. The evolution of carbon dioxide and water is shown in Fig. 4, while the evolution of more complex species is shown in Fig. 5. In general, aliphatic species were not observed.

These graphs show that there has been considerable carbon deposition and that species such as benzene, which was not present in the feed, can be formed on the surface of the catalyst. As expected, the main species detected are aromatics, and very little of the fully hydrogenated species such as methylcyclohexane are seen.

In a typical fixed bed reactor on a chemical plant, the product flow will pass over a significant amount of catalyst that has been added to the reactor but only comes into action as the front end of the bed is deactivated. It is generally assumed that this part of the bed is unaffected by the product gases and is in a similar
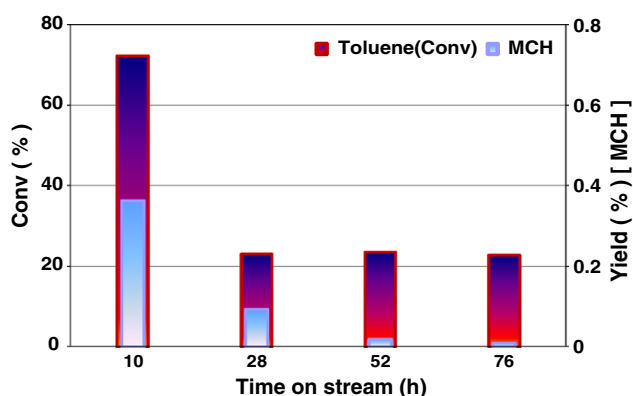

Fig. 3 Deactivation profile for toluene hydrogenation (component part of PyGas). Conditions: 413 K, WHSV 8 h^{-1}, H_2 pressure 5 barg, H_2:PyGas molar ratio = 5, overall pressure 20 barg

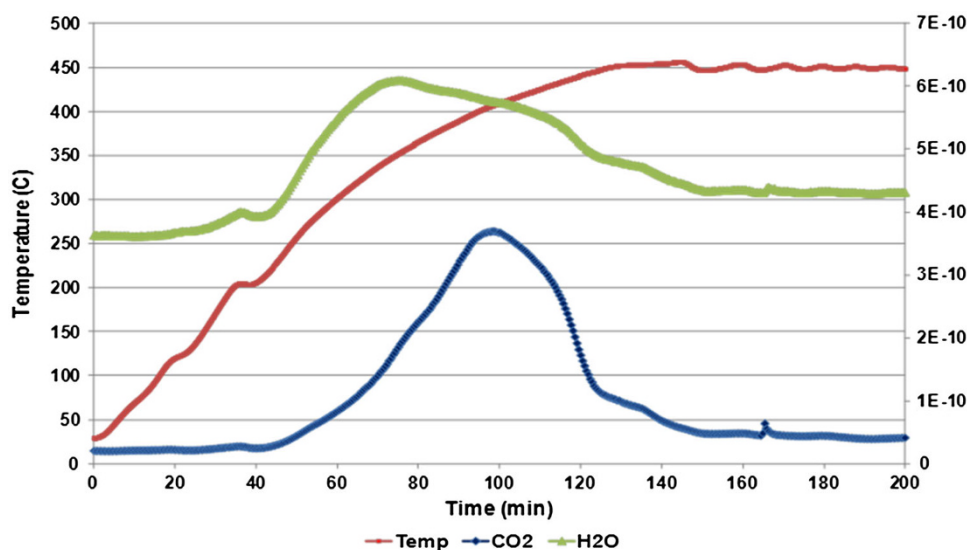**Fig. 4** Evolution of water and carbon dioxide as a function of temperature during TPO

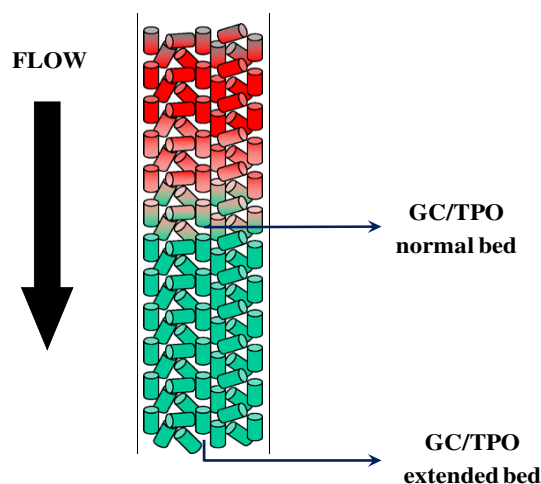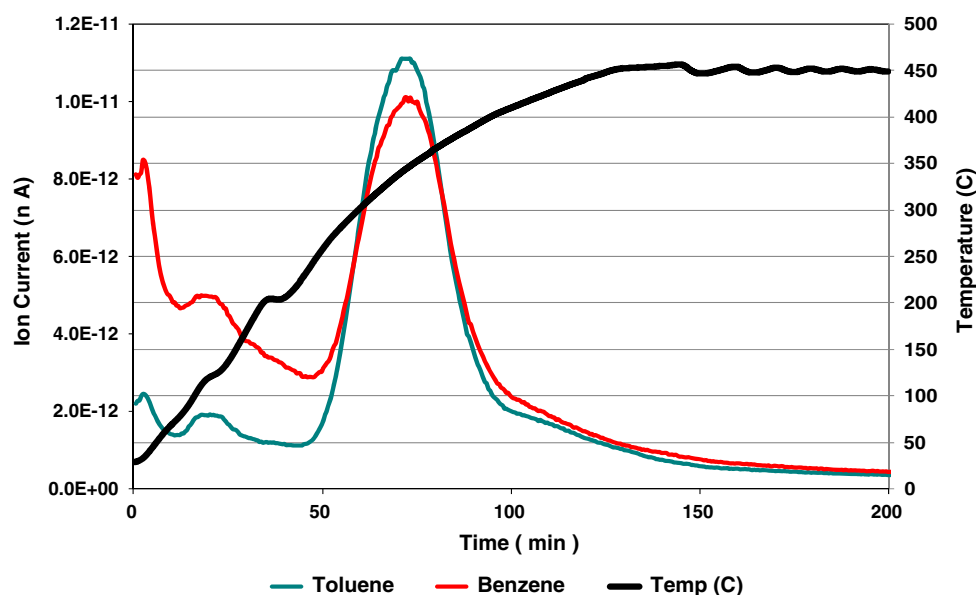**Fig. 5** Evolution of complex species during TPO

Fig. 6 Schematic of full-bed and half-bed reactor tests

FLOW

GC/TPO normal bed

GC/TPO extended bed

Table 4 Conversion of PyGas components at normal-bed and extended-bed positions

Conversion (%)	Extended bed	Normal bed
1-pentene	90.6	87.3
1-octene	98.3	99.3
Cyclopentene	93.8	93.1
Toluene	24.1	23.1
Styrene	99.9	99.9

Conditions: 413 K, 20 barg pressure, 5 barg hydrogen, H_2:PyGas molar ratio = 5

state to fresh catalyst. To test this, the bed of catalyst was extended to double its length and used under the same conditions of flow, pressure and temperature. In this way, it would be possible to generate both GC and TPO data for both the normal bed and the extended bed (Fig. 6).

GC analysis was taken at the bottom of the normal bed and the extended bed to confirm whether the conversion was the same. The results are shown in Table 4 and confirm that the extent of hydrogenation changes very little between the normal-bed position and the extended-bed position as would be expected. In both cases, the catalyst was subjected to the same conditions and was on stream for the same length of time (76 h). TPOs were then run on both the normal and the extended bed. The

normal-bed profiles are shown in Figs. 4 and 5. The extended-bed profiles are shown in Figs. 7 and 8. It is immediately clear that the profiles for the carbon dioxide and water have significantly altered. In Fig. 9, both the carbon dioxide evolution profiles for the normal and extended bed are compared. The carbon dioxide profile for the extended bed reveals that there has been considerable carbon deposition on the "unreactive" part of the bed and this is especially noticeable at the higher temperatures. By 450 °C, carbon dioxide evolution has almost ceased with the normal bed, whereas there is still significant amount of carbon combusting with the extended bed. The water profile is also different. The water evolution from the normal bed covers the same temperature range as the carbon dioxide, although the specific shape is different indicating a variety of carbonaceous species on the surface with different H:C ratios. However, the water profile from the extended bed does not mirror the temperature range of the carbon dioxide. In this case, the water evolution peaks at 350 °C and is almost back to

Fig. 7 Evolution of water and carbon dioxide as a function of temperature during TPO with an extended bed
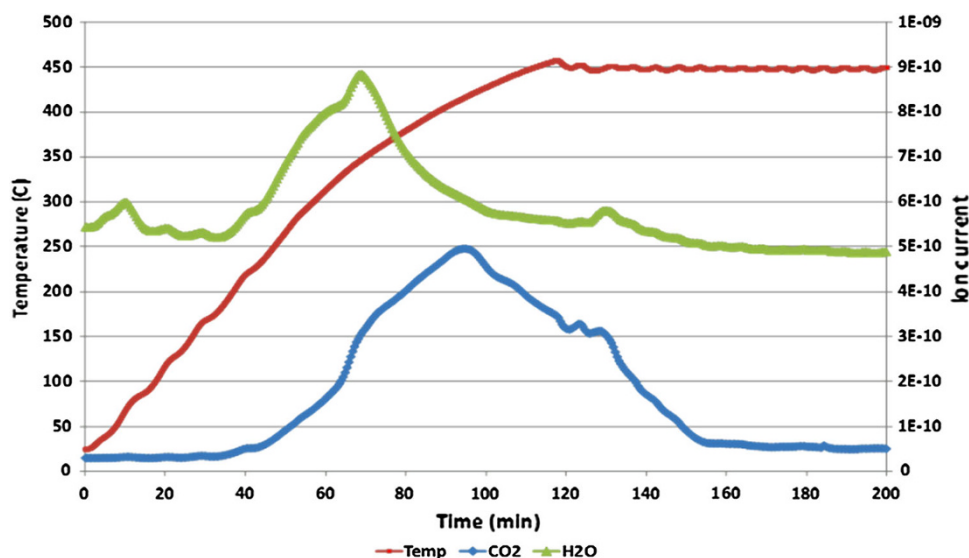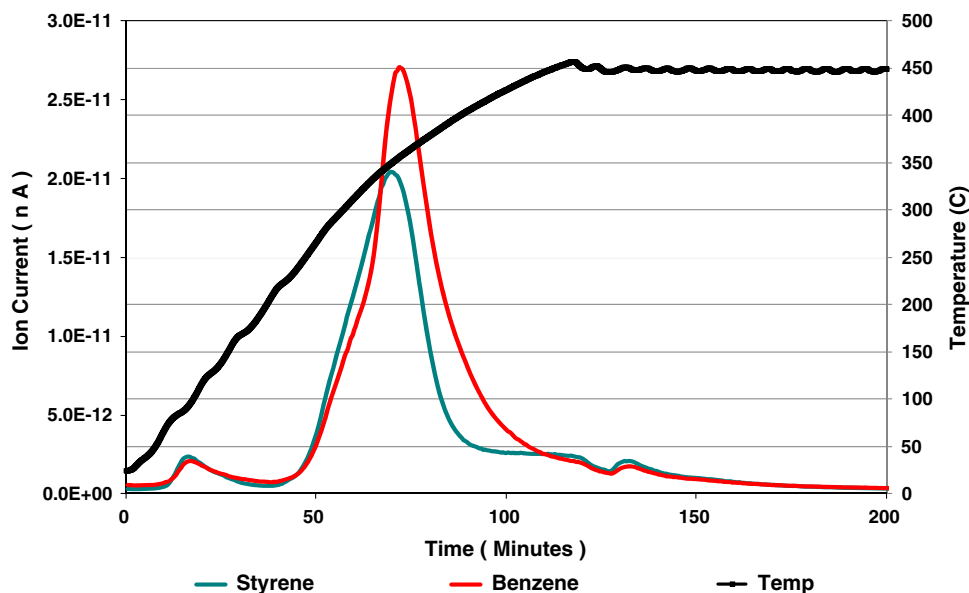

Fig. 8 Evolution of complex species during TPO with an extended bed

baseline by 450 °C. This change can give information related to the C:H ratio of the carbonaceous deposit. The carbonaceous deposit that is combusted at 450 °C on the extended bed produces carbon dioxide but very little water indicating that the deposit has a low H:C ratio, <1 suggesting the formation of polyaromatic or graphitic-like species. Note that this material is deposited in an atmosphere that has much less free hydrogen than that at the start of the bed. Even though much of the organic feed is now saturated, the lower gas phase hydrogen concentration does appear to affect the H:C ratio in a negative way. From the comparison of the water and carbon dioxide profiles, it is clear that on the normal bed the carbonaceous deposit has a much higher H:C ratio over the full profile and hence is easier to combust at lower temperatures.

In Fig. 10, the profiles obtained from benzene and toluene are compared and it can be seen that the extended bed has significantly more aromatic species than the normal bed but there is no evidence for desorption at higher temperatures.

Conclusions

Therefore using this enhanced TPO methodology, we have been able to show that in a standard fixed bed reactor, passing reaction equilibrated gas over fresh catalyst does not necessarily inhibit carbonaceous deposition and that the species deposited may be more deleterious to the catalyst activity than that deposited under reaction chemistry. This has potential implications for catalyst life in the plant and

Fig. 9 Comparison of carbon dioxide and water evolution from the normal (NB) and extended (EB) beds
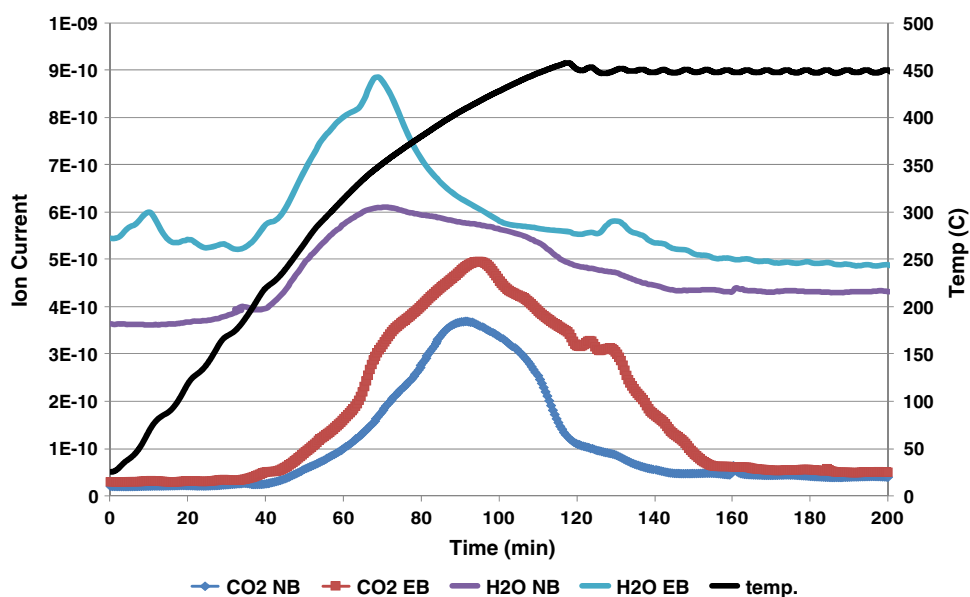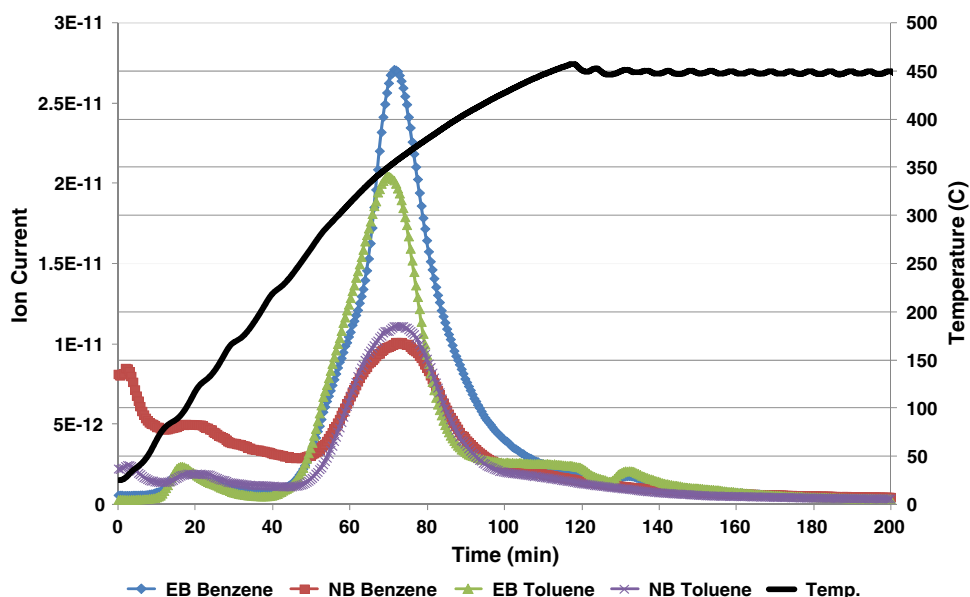

Fig. 10 Comparison of benzene and toluene evolution from the normal (NB) and extended (EB) beds

on the expected activity and selectivity. Using these techniques, a better understanding of the catalyst operating in the plant can be obtained.

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