

**MOLECULAR MODEL OF REFORMING CHEMISTRY
AT REFORMULATED GASOLINE CONDITIONS.**

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ABSTRACT

The Clean Air Act Amendments of 1990 mandate a reduced benzene content and the incorporation of oxygenates in gasoline, and set emissions performance standards for gasoline sold in the nations worst ozone non-attainment areas. These constraints will result in significant changes in operating conditions used in commercial catalytic reformers. Reformer product octanes are expected to drop, throughputs will be reduced, and pressures (and concomitant recycle hydrogen rates) are expected to drop to allow reformers to maintain hydrogen production at reduced severity. These conditions represent a significant change from post-lead-phaseout operation in which product octanes were pushed and pressures were maintained at high levels to increase the run span of semi-regenerative reforming plants.

A pilot plant study was performed to examine the reaction network which exists in a reformer under post-reformulated gasoline operating conditions. Operations were performed at a range of severities using a paraffinic Arabian naphtha as feedstock. Detailed product analyses and careful material balancing allowed construction of a molecular picture of the reforming process at these conditions revealing the nature of yield losses, hydrogen production, and benzene production during the reforming process.

INTRODUCTION

Catalytic reforming is one of the key refinery processes involved in the production of gasoline worldwide. Reforming performs two major functions in the modern refinery: upgrading the octane value of low octane naphthas to make a high octane gasoline blending component; and providing hydrogen for hydrotreating and hydrocracking processes.

The two major reforming technologies used commercially vary by the manner in which the catalyst is regenerated; either periodically (referred to as Semi-Regenerative or semi-regen operation) or continuously (called Continuous Catalytic Reforming or CCR). For the semi-regen plants, the length of the operating cycles between regenerations is an important factor. Bimetallic reforming catalysts (platinum-rhenium on alumina being used most frequently) were developed to extend this cycle length.

Since reforming is a major source of gasoline components, reforming operations are impacted by regulations which constrain the composition of gasoline. As it became necessary to reduce the level of high-octane lead additives in gasoline during the 1970s and 1980s, reformers were required to produce products of higher octane value to compensate for this reduction. Reformers changed in response to these increased demands: improved catalyst systems were developed to allow semi-regen plants to operate with adequate cycle lengths at these more severe

conditions, and the CCR type operation became more cost-effective than it had been at moderate severities.

The Clean Air Act requirements will affect gasoline composition in a manner which is unprecedented in the history of gasoline manufacture. Unlike lead-phaseout, reformers will be likely to operate at lower product octane levels as a result of gasoline reformulation. This is because high-octane oxygenates (such as methyl-tertiary-butyl-ether, MTBE) will be required in areas where reformulated gasoline is produced. Reformulated gasolines must also meet a benzene limit of 1 wt% and must produce fewer hydrocarbon and benzene emissions, requirements which will indirectly limit the total amount of aromatics allowable in such fuels. At first glance, this would appear to make life easier for reformers. However, the reformers must also produce the hydrogen required in other refinery operations and to do so at lower throughputs and lower product octane levels will be a severe challenge. Most refiners are closely examining reducing both operating pressure and the rate of recycle hydrogen circulation to provide additional net hydrogen at the reduced severity conditions. The combined low octane, low throughput, low pressure, low recycle operation is atypical of commonly-practiced reformer operation and is correspondingly an area infrequently examined in reforming studies.

To provide information on the nature of reforming operations under these new conditions a reaction study was conducted. Pilot plant tests were performed using an Arabian Naphtha. The tests were performed using Chevron's commercial Rheniforming F catalyst at 100-150 psig, 1.5 liquid hourly space velocity, and a 2.5:1 molar hydrogen-to-hydrocarbon recycle gas ratio. A continuous reforming pilot plant was employed for the test which consisted of a 1" OD steel tube reactor charged with 80 cc of catalyst.

Samples of the debutanizer overhead ("low-gas") and high-pressure separator gas ("high-gas") were analyzed by packed-column chromatography and their flowrates were measured to provide the rates of C4- product generation. The debutanizer bottoms (C5+ liquid product) were analyzed by capillary column gas chromatography to determine liquid composition.

PRODUCT COMPOSITION AS A FUNCTION OF OCTANE

Figures 1 through 5 provide a schematic molecular view of product composition as a function of research octane number (RON). These figures illustrate the changes in molar composition by showing the number of moles of each molecule present per 10000 gms of original feed. For example, in Figure 1 we see that the in 10000 gms of the original feed are contained roughly 2 moles n-pentane, 3 moles n-hexane, 2 moles iso-hexanes, 1 mole benzene, etc. This feed has a measured RON of 42.9 and is comprised predominantly of C7 and C8 components (about 70 mole % of the feed). The feed is paraffin-rich as well (about 2/3 of the feed molecules) and aromatics-poor (16 mole% aromatics).

Upon conversion to 72.9 RON (Figure 2) a substantial number of the C7+ naphthenes have disappeared along with a roughly equivalent molar amount of paraffins. In contrast, C6 naphthenes are apparently untouched. For the most part, there is a rough agreement between the appearance of aromatics of a given carbon number and the disappearance

of paraffins and naphthenes of that carbon number. For the C7 and C8 molecules, a few more paraffins + naphthenes have disappeared than the number of aromatic molecules which have appeared. C5 and C6 paraffins have each increased by 1 mole per 10000 gm feed. In addition, a mole of benzene and a mole of C11 aromatic (dimethyl indan?) have appeared where no corresponding conversion of feed paraffin or naphthene seems to have occurred.

When product octane is raised to 83.5 RON (Figure 3), disappearance of C8+ paraffins is the dominant reaction. 75% of the C7 paraffins present in the feed still remain. Additional C5 and C6 paraffins are produced. The product is now 50 mole-% aromatics.

By 94.7 RON (Figure 4), virtually all of the C9+ paraffins and 80% of the C8 paraffin have been converted. Only about half of the C7 paraffins have been converted, however. Of the naphthenes, only the C6s remain. The largest gains in the aromatics are seen in the C8+. The liquid product is 62 mole % aromatics.

In raising product octane to 100 RON (see Figure 5), C7 paraffin conversion finally begins to accelerate significantly reaching a level of 75% conversion. The C6 naphthenes are finally converted. More C5 paraffins are generated and the first signs of disappearance of heavy aromatics is seen (destruction of a C10 aromatic). The product is over 70 mole % aromatic with the balance being entirely composed of C7-paraffins.

REACTION CHEMISTRY

By matching the appearance of various molecules with the disappearance of others as the reaction proceeds, one may predict the reaction network which is occurring as severity is increased.

In order to produce such a network, certain assumptions are necessary. The assumptions used herein are as follows:

- 1) 100% of the converted naphthenes produce an aromatic of the same carbon number.
- 2) The remainder of the aromatics produced for a given carbon number are derived from dehydrocyclization of a paraffin of the same carbon number.
- 3) Other imbalances in the number of aromatics of a given carbon number are caused by side-reactions of aromatics which result in changes in carbon number of the aromatics.
- 4) Converted paraffins above those needed to form aromatics contribute to light product formation.

Figure 6 provides the net reaction network which evolves from the application of these reaction rules to the changes in product composition provided above. In going from 43 to 73 RON (first column in Figure 6), both dehydrogenation and dehydrocyclization share in the production of aromatics and hydrogen (numerals in circles at the bottom right-hand corner of each section of the table indicate the total contribution to hydrogen production for given set of reactions - for instance at 73 RON, dehydrogenation contributes a total of 39 moles H₂

while dehydrocyclization contributes a total of 40 moles H₂). C₇ paraffin reactions are limited to isomerization and cracking (all of the toluene production is explainable from naphthene dehydrogenation). One molecule of C₈ paraffin is also left to produce gas while four C₈-paraffin molecules produce aromatics. There is an additional net aromatic reaction needed to explain the presence of benzene and a C₁₁ aromatic - this is assumed to occur through disproportionation (or transalkylation) of a C₈ and a C₉ aromatic to a C₁₁ plus a C₆ aromatic followed by a dehydrogenation of the monoaromatic C₁₁ to a diaromatic C₁₁.

Between 73 and 84 RON, dehydrocyclization of C₈ and C₉ paraffins is the primary source of aromatics and hydrogen. The t-butyl-benzene is converted and a diethyl-benzene appears in its place. Gases are produced from C₇ to C₁₀ paraffins.

Between 84 and 95 RON, dehydrocyclization continues with participation of C₇ paraffins in the reaction scheme. The gas production continues to pick up and most of the cracked paraffins must now experience multiple cracking events in order to explain the gas yields. Two additional reactions are needed to explain the redistribution of aromatics: the disappearance of a diethyl-benzene with the appearance of a naphthalene; and an additional benzene is produced which is matched with the disappearance of propyl-benzene.

Between 95 and 100 RON the cracking reactions take over. Some additional aromatics are generated from C₆ naphthene conversion and dehydrocyclization, but gas production takes a steep upturn and most of the converted molecules contribute to the cracking reactions. In order to explain the gas production, almost 90% of the cracked molecules must experience multiple cracking events. The hydrogen produced from the dehydrogenation and dehydrocyclization is consumed by the large number of cracking events.

BENZENE PRODUCTION

For reformulated gasoline production, it is of specific interest to understand the origin of benzene in reformate. The evidence above shows that substantial benzene is produced prior to any significant conversion of C₆ naphthenes. Figure 7 presents the conversion data on C₆ components versus octane for a range of conditions and catalysts tested on this feedstock (including data from various catalysts at pressures ranging from 100-200 psig, and recycle rates ranging from 2.5 to 3.5 molar H₂/HC, at 1.5 LHSV). This data confirms that under a broad range of conditions, benzene is produced from sources other than C₆ naphthenes or paraffins. It is true that benzene production does turn up considerably with the conversion of C₆ naphthenes above 90 RON, thus removal of these materials from the feedstock does have a significant impact on benzene production. However, it is also true there is considerable benzene produced without the contribution from C₆ precursors and even complete removal of C₆ components from the reformer feed may not totally eliminate benzene production.

Examination of the relationship between production of benzene and other aromatics shows that benzene production appears most closely correlated to toluene and naphthalene (see Figures 8 and 9). A possible interpretation is that benzene is produced from transalkylation reactions which increase the amount of aromatics with a low degree of

substitution (benzene, toluene and naphthalene) at the expense of those with a higher degree of substitution (poly-methyl-, or poly-methyl-alkyl- benzenes). The most likely sources of benzene from transalkylation would be aromatics with the largest side chains and/or highest degree of substitution.

CONCLUSIONS

The model illustrates the progression of reactions which occur in reforming of a paraffinic naphtha. The three major classes of reactions are naphthene dehydrogenation, paraffin dehydrocyclization, and paraffin cracking. As expected, naphthenes convert most readily generating aromatics primarily of the same carbon number. Hydrogen production from this conversion is about 75% complete by 73 RON and accounts for about half of the hydrogen produced at this severity. Additional aromatics and hydrogen are generated from the dehydrocyclization of paraffins. The selectivity of conversion of paraffins to aromatics increases with increasing carbon number - 20% for C7s, 60% for C8s, 85% for C9+. C7 paraffins convert slowly until higher severities and appear to be responsible for about 2/3 of the gas formed at 100 RON. Other reactions have a very minor role in explaining the distribution of products observed. Benzene production is observed to begin well before significant disappearance of C6 naphthenes occurs which implies that removing C6s from reformer feeds while substantially reducing benzene production will not totally eliminate it from reformer products.

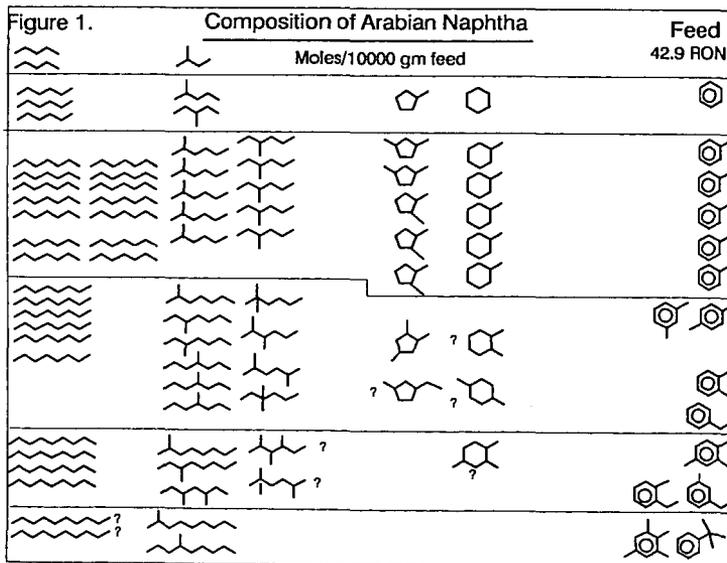
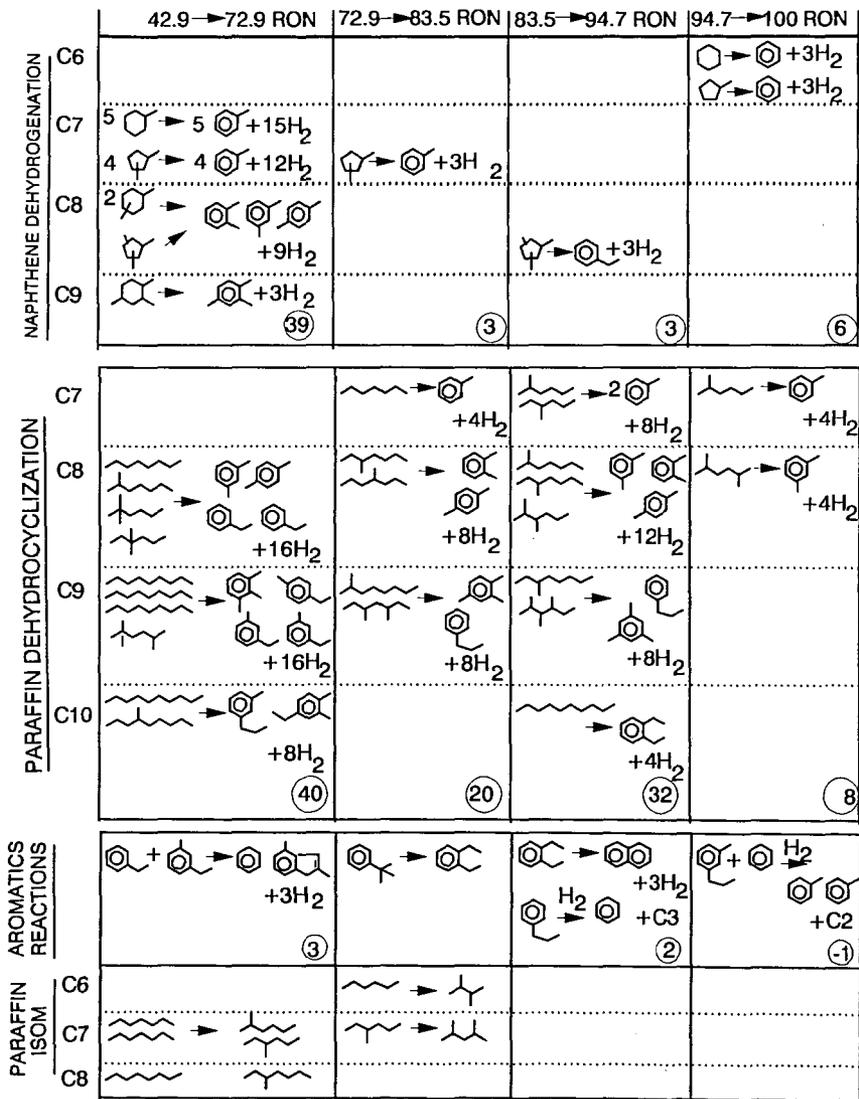


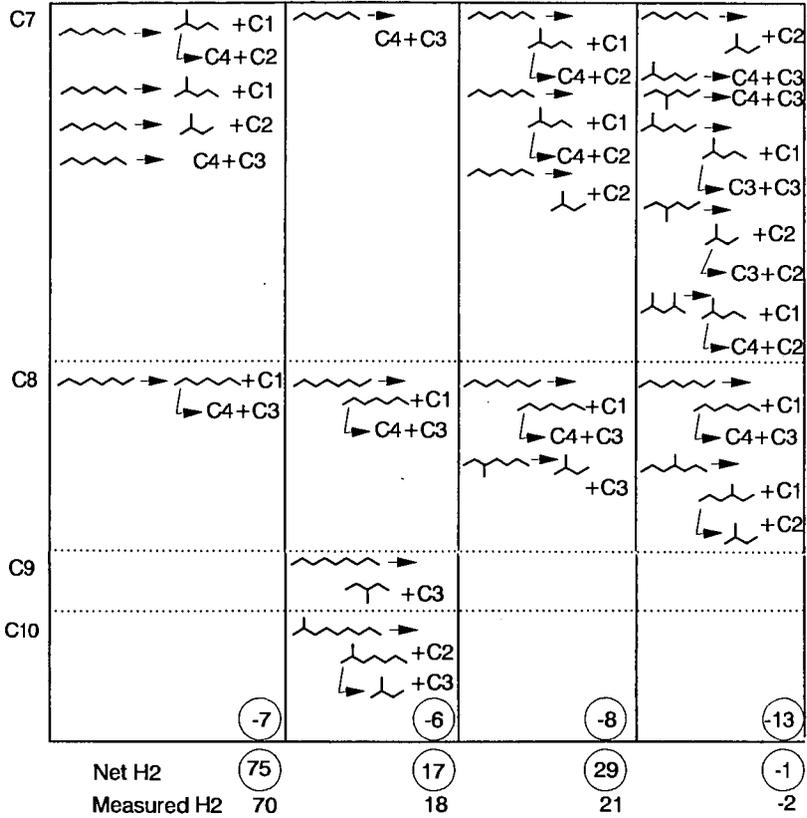
Figure 2.		Composition of 72.9 Octane Reformate				Product
		Moles/10000 gm feed				72.9 RON

Figure 3.		Composition of 83.5 Octane Reformate				Product
		Moles/10000 gm feed				83.5 RON

Figure 6
Reforming Reactions as a Function of Severity



PARAFFIN CRACKING AND HYDROCRACKING



C4- Yields above are different from those actually produced as noted below (differences caused by C balance).

An extra C1 is shown.

A C3 should be a C2.

(In balance)

2 additional C1s needed.

Figure 7.
Conversion of C6 Components
Versus Reformate Octane

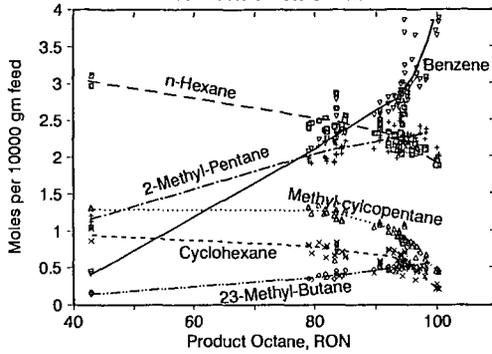


Figure 8.
Correlation Between Reformate
Benzene and Toluene Content

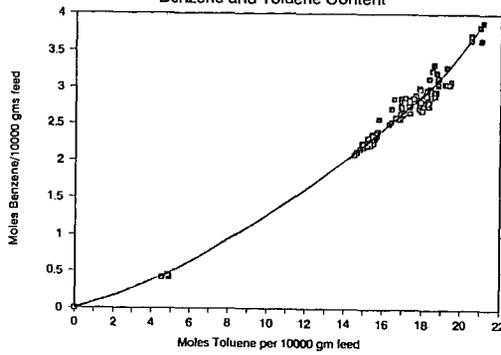


Figure 9.
Correlation Between Reformate
Benzene and Naphthalene Content

