

## REACTIONS OF HYDROGEN DURING HYDROPROLYSIS PROCESSING OF HEAVY ENDS

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### INTRODUCTION

When heavy oils are subjected to pyrolysis in the presence of hydrogen, cracking to lower molecular weight compounds is accelerated and production of coke is inhibited compared to the case in which an inert atmosphere is present.<sup>(1-3)</sup> It has previously been reported that at very high hydrogen concentrations ( $>10^3$  vol/vol) production of coke is virtually eliminated.<sup>(4)</sup> Others have reported that the presence of hydrogen improves liquid hydrogen yield when cracking residual oils.<sup>(5)</sup>

In the course of our investigations considerable attention has been given to changes in molecular structure and product characteristics. By comparing results with those obtained in the absence of hydrogen an understanding of the reactions of hydrogen is beginning to emerge. In this paper, an attempt is made to categorize the major reactions of hydrogen and to justify these reactions in terms of the observations made.

### Chemical Effects Observed in Hydropyrolysis

#### Reduction of Coke Formation

The most obvious and perhaps most important effect of hydrogen is the inhibition of coke forming reactions. In hydropyrolysis of tar sand bitumen, which yields 16-20% coke in delayed coking processes, conditions exist in which virtually no coke is produced.<sup>(2-4)</sup> Representative results are shown in Table 1.

Table 1

#### Product Yields from Coking and Hydropyrolysis of Tar Sand Bitumen

	SUNNYSIDE BITUMEN		ATHABASCA BITUMEN	
	Coking	Hydropyrolysis (Coiled Tube)	Coking	Hydropyrolysis (Verticle Tube)
	WEIGHT PERCENT YIELDS			
Gas	8.9	27.0	7.5	1.7
Liquid	71.0	73.0	76.5	93.7
Coke	20.1	NIL	16.0	4.6

When model compounds are subjected to hydropyrolysis there is no evidence for products of higher molecular weight than the starting material.<sup>(2-6)</sup> Thus, addition and condensation reactions are completely inhibited. The chemistry of coke forming reactions and the inhibition of these reactions during hydropyrolysis are discussed in greater detail in a companion paper.<sup>(7)</sup>

### Reduction of Dehydrogenation of Naphthenes

It has also been observed that during hydropyrolysis little change in total aromatic carbon occurs ( $C_a = .22$  for products and  $.19$  for feedstock) while coking dramatically increases the aromatic carbon ( $C_a = .30$ ).<sup>(8)</sup> It has also been observed that hydropyrolysis products possess a higher fraction aromatics and lower content of diaromatics than do coker products<sup>(3)</sup> (see Table 2).

Table 2

Compound Type Analysis of Total Products\*  
From Asphalt Ridge Bitumen

	<u>Coking</u>	<u>Hydropyrolysis</u>
Saturates	52.4	59.4
Monoaromatics	8.4	12.0
Diaromatics	6.1	4.4
Poly-Polar Aromatics	33.0	24.1
Gas/Liquid/Coke (weight percent)	4/81/15	17/83/0
Avg. M.W. Liquids	321	336

\*Values given are on a feed basis; gas production is lumped into the saturates portion and coke production is lumped into the poly-polar aromatics fraction.

From the data above it is not possible to tell whether the principal effect of hydropyrolysis is to inhibit the denydrogenation of naphthenes to form aromatics or that hydrogenation of condensed aromatics to form monoaromatics is occurring. As will be shown below both appear to be happening. NMR data taken on an Athabasca bitumen and the liquid products from hydropyrolysis (93% yields) suggests that the fraction of monoaromatic carbon increases with hydropyrolysis processing. For the Athabasca case the fraction aromatic carbon ( $f_a$ ) declines from 0.35 to 0.28 while the fraction aromatic hydrogen ( $H_a$ ) increases from .04 to .05, clearly showing lower levels condensation and/or a lower degree of alkyl substitution.

### Hydrogenation of Aromatics and Olefins

The observation that total aromatic carbon remains virtually constant (or in some cases declines) while the distribution shifts from polycondensed aromatics toward monoaromatics strongly suggests that polycondensed aromatics are being hydrogenated. In hydropyrolysis where coke formation is small the amount of polyaromatics in the feed that can be accounted for by loss to coke is limited.

In an attempt to ascertain whether or not aromatics are in fact being hydrogenated during hydropyrolysis, a mixture of 5% naphthalene in n-hexadecane was hydrolyzed at 540°C and 2000 psig H<sub>2</sub> and 30 sec residence time. Approximately 6% of the naphthalene was converted to tetralin. The identity of tetralin was confirmed by mass spectroscopy. Calculations of the thermodynamic equilibrium between saturates and aromatics reveal that only the mono-aromatics are strongly favored at these conditions. In the tetralin-naphthalene system and at the reaction conditions given the equilibrium concentration for tetralin is 0.3 mole fraction (in the absence of cracking of tetralin).

As with aromatics there is also a strong tendency to hydrogenate olefins. It has previously been reported<sup>(1,2)</sup> that olefins content is reduced in hydrolysis by as much as 50-80% compared to thermal cracking in an inert atmosphere. At higher pressure  $\geq$  2000 psig H<sub>2</sub> terminal olefins are virtually absent from the products of hydrolysis of n-hexadecane. It is noteworthy that in the experiment in which naphthalene was added to n-hexadecane the C<sub>5</sub>-C<sub>15</sub> paraffins to olefin ratio declined to 3.0 compared to 5.7 for the case when n-hexadecane was hydrolyzed in the absence of naphthalene. This data suggests that aromatics compete with olefins for available hydrogen during saturation.

An interesting effect of the presence of naphthalene was to reduce the conversion of n-hexadecane at constant reaction conditions. When other unsaturated bonds such as olefin, carbonyl, or sulfoxide are added to the system a similar reduction in the level of cracking of n-hexadecane is observed<sup>(11)</sup>. Also, the greater the concentration of unsaturated bonds added, the greater is the production of olefins from n-hexadecane. This inverse relationship between concentration of unsaturated species and cracking rates of saturated species clearly suggests the existence of competitive reactions.

#### Promotion of Dealkylation

Hydrolysis appears to promote dealkylation reactions. Evidence for dealkylation at the ring can be seen from NMR data for the Athabasca case in which the fraction of aliphatic hydrogen alpha to an aromatic ring is reduced from 0.27 to 0.21. In coking, by contrast, dealkylation at the benzylic position is generally favored and the fraction of aliphatic hydrogen alpha to the ring tends to increase. Further, when pentane soluble maltenes from tar sand bitumen are subjected to hydrolysis the products are shown to contain 11% pentane-insoluble material.<sup>(8)</sup> This material is characterized as highly dealkylated material (H/C  $\geq$  0.9).

In an attempt to examine the chemistry of dealkylation, a mixture of 20% n-propyl benzene in n-hexadecane was subjected to hydrolysis at 2000 psig, 540° and 30 sec residence time. In order to separate the hydrogen pressure effects from the total pressure effects a second run was made with a partial pressure of 500 psi H<sub>2</sub> and 1500 psi He. Reaction conditions were otherwise identical. Results are shown in Table 3. As the concentration of aromatics is increased or the partial pressure of hydrogen is decreased, the level of conversion of both reactants is decreased. These results are consistent with those stated above, which shows that hydrogen accelerates the cracking reactions.

The results show that dealkylation at the ring position is promoted by the presence of hydrogen. The ratio of benzene to toluene varies directly with the partial pressure of hydrogen. These results are consistent with hydrodealkylation chemistry in which attack by a hydrogen atom at an ipso position results in cleavage of the alkyl-aromatic bond.

The pressure of aromatic to the system reduces the level of olefin saturation but not as much as a reduction in the partial pressure of hydrogen. These results are consistent with those obtained when naphthalene was added to the system. Thus, the aromatic ring appears to act as a sink to deplete the population of H\* in the reaction zone.

#### Hydropyrolysis Promotes a Broader Distribution of Products

The reduction in the C<sub>4</sub>/C<sub>1</sub> ratio seen in Table 3 is consistent with an increasing thermal effect and decreasing hydropyrolytic effect. It is noteworthy that in hydropyrolysis C<sub>3</sub>-C<sub>4</sub> gas production is enhanced while methane production is greatly reduced in relationship to coking<sup>(3)</sup> (at constant conversion). Further, the boiling point distribution of hydropyrolyzate is broader than with coker distillate from the same feed.<sup>(4)</sup> This is illustrated in Figure-1 which also compares the boiling point distribution of hydropyrolysis products with virgin crude oil. These results suggest that hydrogen plays an important role in free radical transfer (propagation) reactions resulting in a wider variety of cracking events than is the case with coking.

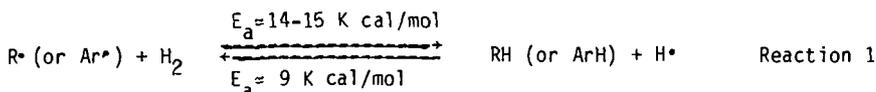
Table 3

#### Hydropyrolysis of *n*-Propylbenzene in *n*-Hexadecane

	Feedstock (Atmosphere)		
	<i>n</i> -hexadecane (H <sub>2</sub> )	20% <i>n</i> -propyl benzene in <i>n</i> -C <sub>16</sub> (H <sub>2</sub> )	20% <i>n</i> -propyl benzene in <i>n</i> -C <sub>16</sub> (.25H <sub>2</sub> , .75H <sub>e</sub> )
Conversion			
<i>n</i> -hexadecane	88.5	83.6	79.4
<i>n</i> -propyl benzene	---	31.0	26.6
Product	Product Yield (percent of <i>n</i> -propyl benzene converted)		
benzene	0	13.7	8.9
toluene	0	14.7	16.6
styrene	0	12.7	6.4
ethylbenzene	0	52.8	52.4
(unidentified	100	6.1	15.7
or not listed)	100	100.0	100.0
	<u>Other Indicators</u>		
C <sub>8</sub> Paraffin/Olefin	4.3	3.2	0.9
C <sub>4</sub> /C <sub>1</sub>	2.1	1.9	1.5

## Reactions of Hydrogen

Molecular Hydrogen - The principal reaction of molecular hydrogen is as a reactant in the general metathesis reaction (1) (activation energies given are for the alkyl radical):



The significance of this reaction to hydropyrolysis cannot be overstated. It is through this reaction that free radicals are saturated. Equally important is the fact that hydrogen atoms are produced. Production of hydrogen atoms is critical to hydropyrolysis chemistry and the mechanism shown in the above reaction provides a means for production of hydrogen atoms at modest temperatures. Good contact between hydrogen and the free radicals, is important and homogeneous, vapor-phase reaction conditions favor this reaction. Hydrogen abstraction reactions are thought to occur at appreciable rates for alkyl hydrogen at 410° and for aromatics at about 425°C during coking.<sup>(7)</sup> On this basis and considering relative bond dissociation energies, it may be predicted that the forward metathesis reaction occurs at significant rates at temperatures above about 435°C. Indeed many hydrovisbreaking processes operate at temperature regimes just above this temperature<sup>(9)</sup> and the metathesis reaction is probably important to these processes as well.

The effect of the metathesis reaction can be seen in the observations listed above. First, dehydrogenation of naphthenes is reduced because molecular hydrogen serves the function of providing hydrogen to saturate free radicals. Second, aryl free radicals are saturated before they can add to arenes forming thermodynamically stable aryl-aryl bonds. The reaction of aryl radicals with arenes is thought to be an elementary step in coke formation<sup>(7)</sup> and suppression of coke is due in part to reaction-1. Third, alkyl radicals are saturated before they can undergo  $\beta$ -scission and overcrack. There is actually a reverse argument to this latter point in which the reverse of reaction-1 results in accelerated cracking. The net effect is that molecular and atomic hydrogen act, in effect, as vehicles for the transfer of free radical resulting in a more random point of cracking than is experienced with thermal cracking. Thermal cracking is more energetically controlled and as a result the products tend to be more selectively distributed between very light gases or heavy gas oils. In hydropyrolysis, significant amounts of LPG and middle distillate are generated as discussed above.

### Atomic Hydrogen

Evidence for the presence of atomic hydrogen in hydropyrolysis is clear from the observations presented. Based on reaction-1, the population of hydrogen atoms would tend to increase as the overall population of free radicals increases and as the concentration of hydrogen (gas/oil ratio) increases. Reactions of atomic hydrogen can be grouped into two general types: (i) free radical hydrogen addition and (ii) free radical hydrogen abstraction reactions.

The hydrogen addition reactions are characterized by attack on unsaturated bonds, olefins and aromatics, to form alkyl or cyclohexadienyl-type radicals, respectively. These radicals subsequently undergo metathesis

reactions with hydrogen to saturate the radical and regenerate the hydrogen atom. The presence of unsaturated bonds tends to decrease the overall population of  $H^{\bullet}$  as evidenced by the reduced cracking rates for n-hexadecane when unsaturated bonds are present.

If hydrogen adds to a substituted aromatic carbon it is probable that ring dealkylation will occur due to the relative strength of the C-H bond vs. the C-C bond. The same effect is not true for aryl-aryl bonds, however, which are thought to be stronger than the corresponding C-H bond.<sup>(10)</sup> If hydrogen adds to an unsubstituted aromatic carbon and a hydrogen is eliminated before the free radical can be hydrogenated an unproductive event occurs which cannot be observed in the products. This reaction may, however, account for the sink for  $H^{\bullet}$  observed when aromatics are present.

Hydrogen abstraction reactions are also important to hydroperolysis results. Hydrogen abstraction, or the reverse of reaction-1, results in a free radical which can subsequently undergo  $\beta$ -scission to crack the molecule in two. The fact that the rate of cracking of n-hexadecane depends upon the  $H^{\bullet}$  concentration testifies to the importance of this reaction. The broad distribution of the products as well as the relatively high concentration of LPG range gases indicates that a less selective and more random cracking is occurring. This is probably due to the less discriminating nature of  $H^{\bullet}$  abstraction vs. free radical abstraction in the absence of hydrogen.

#### SUMMARY

In summary, both molecular hydrogen and atomic hydrogen are reactants in hydroperolysis of residual oil. The reactions of hydrogen postulated can account for the major differences between pyrolysis in an inert atmosphere and hydroperolysis. Coke is inhibited through saturation of aryl radicals by molecular hydrogen and through hydrogenation of vinyl aromatics (and olefins) by addition of  $H^{\bullet}$ . Cracking rates are enhanced through hydrogen abstraction reactions. Product distribution is broadened through less energetically discriminating free radical formation. Hydrogen also seems to act as an effective heat transfer fluid and as a diluant to inhibit bimolecular addition or condensation reactions relative to unimolecular cracking reactions. In time, as the relative kinetics of these reactions become better understood specific process development routes may become apparent. The applicability of hydroperolysis to upgrading feedstocks from a variety of sources and compositions should likewise become more apparent.

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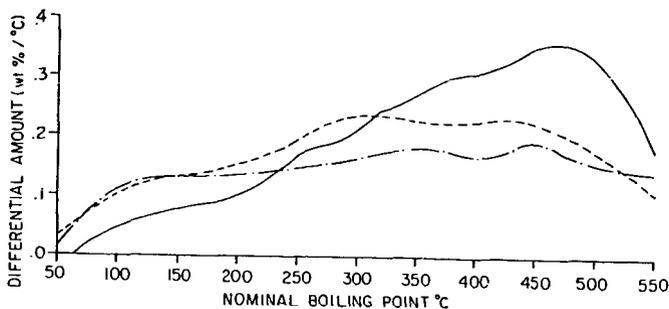


Figure 1. Distillation curves for selected tar sand products and Wilmington crude oil: Asphalt Ridge coker distillate (97% distillable, 27° API) (—); Asphalt Ridge hydropyrolysis condensables (85% distillable, 25° API) (---); Wilmington, CA crude oil (65% distillable, 20° API) (- · -).