Paraffin cracking is much faster than aromatics dealkylation. Paraffins severely crack in the HDA environment, the main products being methane and ethane. The overall reaction of paraffin cracking can be described as (in case of an octane isomer):

$$C_8H_{18} + (\tfrac{1}{2}x+3)\,H_2 \rightarrow x\,CH_4 + (-\tfrac{1}{2}x+4)\,C_2H_6$$

Hydrocracking of paraffins is strongly exothermic as many bonds are broken. Precautions have to be taken when nonaromatics are fed together with aromatics. The enormous heat release of paraffin cracking can cause runaways when sudden increases of the nonaromatics content of the feed do occur.

One major side reaction in dealkylation of alkylated aromatics is the production of diphenyl:

$$2\,C_6H_6 \rightleftarrows (C_6H_5)_2 + H_2$$

Besides, a whole spectrum of heavy components can be found, including naphthalene, methyldiphenyl, diphenylmethane, indane, fluorene and terphenyls. Due to the addition of a large excess of hydrogen, the selectivity of the hydrodealkylation is normally over 95%, even at high conversion. Data on the production of heavy components during the dealkylation of toluene is given in table II.3. Note the large influence of the hydrogen/aromatics ratio on both the amount and composition of the heavies fraction.

Reaction data:		
Temperature (°C)	800	800
H2/Toluene ratio	5.5:1	1.6:1
Residence time (s)	6	3.8
Conversion (%)	96	60
Yield of heavies (m%)	5.3	9.0
Fraction boiling 230-420°C in heavies	100	>96
Composition of heavies:		
α-Methylnaphthalene	-	3
Diphenyl	86	37
Methyldiphenyl	2	30
Diphenylmethane	-	5
Fluorene	10	11
Anthracene/Phenanthrene	1	2
m-Terphenyl	-	1
Fluoranthene	1	-
unidentified	-	11

Table II.3: Some data on toluene dealkylation (Asinger, 1971).

2.2.2 Thermodynamics

The thermodynamic equilibria of a few reactions determine the operation window of a HDA reactor. In figure II.2 this thermodynamic window is given for the dealkylation of pure toluene. Within the temperature interval given in this figure, the equilibrium of the toluene dealkylation reaction favors the formation of benzene (equilibrium line at the right upper side of the figure). With rising the temperature, the equilibrium constant lowers, which implies that

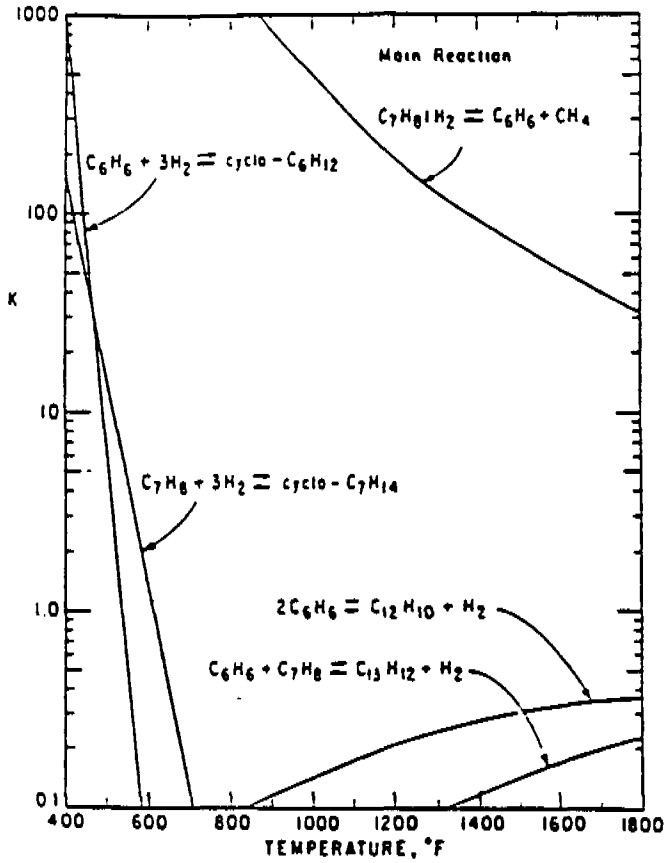

Figure II.2: The thermodynamic window for the HDA reactor (Kooke, 1990).

the theoretical maximum attainable conversion lowers with rising temperature. On the contrary, the kinetic rate will of course rise with rising temperature. A combination of both effects determines the ultimate conversion: thermodynamics determines the driving force, kinetics the speed to attain equilibrium. Figure II.3 shows the equilibrium conversion of toluene as function of temperature for several hydrogen/aromatics ratios (called α in this figure). From this graph it can be concluded that lowering the hydrogen/aromatics ratio lowers the thermodynamic possible conversion. Okkersen (1984) concluded from this graph to use hydrogen/aromatic ratios above 2.

The lower temperature bound of the HDA operating window is determined either by kinetics or by hydrogenation reactions. For the thermal dealkylation process the lowest operating temperature (about 550°C) is determined by the kinetic rate. At still lower temperatures the reaction is that slow that extremely long residence times are necessary. When dealkylating using a catalyst, the lowest reaction temperature must be above about 450°C to prevent hydrogenation of benzene and toluene into cycloparaffins, which will crack further to small paraffins.

The upper temperature level of the dealkylation reaction is determined by two negative side reactions. First, as can be seen in the right lower part of figure II.2, when operating at higher temperatures, the equilibrium constant for the production of heavies rises. Thus, at higher temperatures, the selectivity towards the production of benzene will lower. Second, at higher temperatures, the coke producing reactions such as:

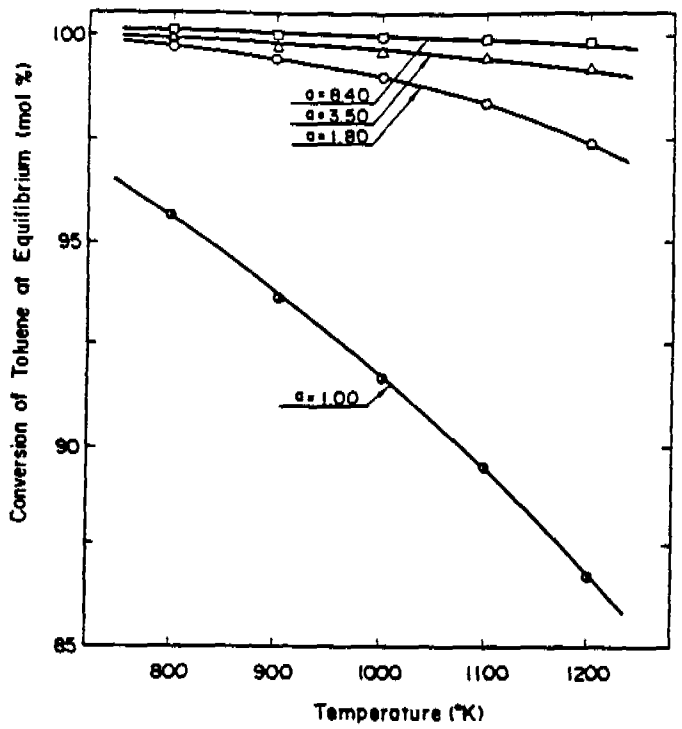

Figure II.3: The toluene dealkylation equilibrium for severall hydrogen/aromatics ratios (Yamada and Amano, 1983).

$$CH_4 \rightarrow C(s) + 2\ H_2$$

will start. These coke producing reactions are highly exothermic, causing a runaway. Coke deposition in the heat train will trouble heat transfer, necessitating cleaning shutdowns. Considering thermodynamics of the coke reaction the following criteria to prevent coke formation was developed:

$$\frac{P_{H_2}^2}{P_{CH_4}} > K$$

in which: p_{H2} = hydrogen partial pressure [atm];
P_{CH4} = methane partial pressure [atm];
K = threshold value for coking to occur.

The threshold value of the criteria changes with temperature. See table II.4.

COKE ?

	K
800 K 527°C	0.706 atm
900 K	3.1 atm
1000 K	10.25 atm

627°C
727°C

Table II.4: The equilibrium constant for methane cracking (Asselin, unknown).

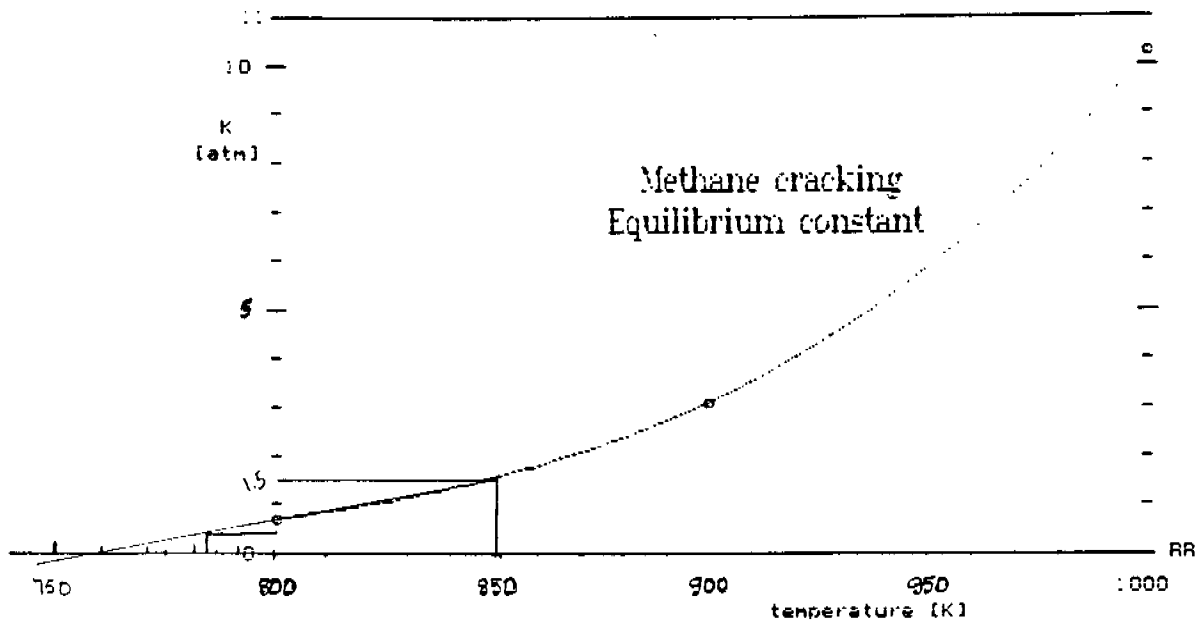

Figure II.4: The equilibrium constant for methane cracking (Asselin, unknown).

2.2.3 The Process Flowsheet: An Introduction

The above presented chemistry clearly shows that the process flowsheet (figure II.5) can be simple. It contains a reaction section and a small separation section. The separation system can be small as the main components in the process system are a C_{6+} fraction mainly containing aromatics and a light gas fraction containing hydrogen, methane and ethane. Separation of these two main fractions can be done by a simple flash.

Fresh aromatic feed is mixed with a recycle stream from the bottom of the benzene tower, containing unreacted feed and heavy byproducts (biphenyl, heavies). This aromatic stream is injected into the hydrogen recycle gas and brought to reaction temperature (600-700°C) by crossing with the reactor outlet stream and by a fired

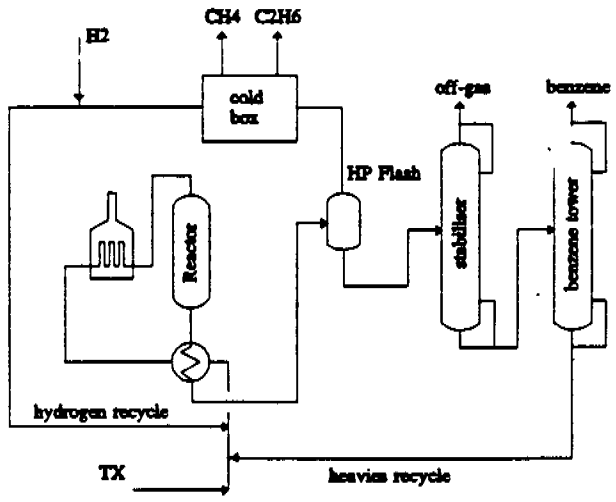

Figure II.5: A simplified flowsheet of the HDA Process.