Higher Olefin Process Esso

Basis of Design

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1. Description of the Design

Exxon's Flexicoking process upgrades vacuum residue oil and splits it up into Gas, LPG, Naphtha over the top, Light Koking Gas Oil (LKGO) as a side stream ~~and~~ Heavy Koking Gas Oil (HKGO) over the bottom. The said top stream is passed through a desulfurizing step and then through a deethanizer and debutanizer sequentially. The deethanizer withdraws C_1-C_2 hydrocarbons from this stream (which are sold to the Gasunie). The debutanizer splits this stream into LPG (C_3-C_4) over the top and naphtha over the bottom. The subject of this assignment lies in the top stream of the Flexicoking process, especially in the stream ~~entering~~ of feed the debutanizer.

This stream contains about 160 components, some known and some unknown. The typical value of this stream, which after some steps ends up as fuel oil, is 100-150 $/ton. The naphtha, however, contains α-olefins which have a value of 1000-1500 $/ton and find themselves in a growing market **[1]**, so there is some profit to be expected when these materials can be isolated. Furthermore, the α-olefins can be used together with the internal olefins, also present in the naphtha, to produce detergent intermediates for the soap industry, with a price range of about 1500-2000 $/ton. We chose detergent intermediates because this product has many applications and therefore a larger market compared to end products such as alcohols (surfactants) and acids (detergents).

It is the object of this design to separate all the linear olefins from the naphtha and use these components as reactants in a process to upgrade these olefins from the C_3-C_6 range to the C_{10}-C_{16} range, as commonly used in detergent, within the economical window provided by Exxon.

The design, which will be done in ChemCAD III, starts with modeling the stream of naphtha through lumping components (see paragraph 2.4 and 3.1.1). Then, attention will be given to the operating conditions of the debutanizer, already present in the current process (see paragraph 2.1.1). From there on the modeling of first the separation and later on the reaction starts. The design will be concluded by integrating the entire process and calculating the economics that come along with the process.

The design can be evaluated at two points: after the separation and after the reaction. In both cases an evaluation will be made of the profits (this is because the products from both the separation and reaction have a profitable market).

2. Process definition

The design consists of three stages: a debutanizer, a separation section and a reaction section . These stages are outlined in the following paragraphs.

2.1 Process concept chosen

Due to the large streams (40-70 tons/hr), it is more favorable to operate the process continuously.

2.1.1 Debutanizer

Because of the need of C_3-C_6 olefins in manufacturing detergents by oligomerization, the light ends of the bottom stream (C_5-C_6) have to be combined with the top stream (C_3-C_4). This can be done by choosing a lower reflux ratio for the debutanizer and a higher operating temperature by simply increasing the MPA (methyl propyl amine) fractionator stream. The MPA fractionator is responsible for the heat duty in the reboiler. Another advantage is that the heavy ends can continue their normal route through the process. This however at the cost of higher MPA fractionator costs.

2.1.2 Separation

The object of the separation is to obtain α- and internal olefins with the highest possible recovery and purity. To accomplish this, the said components have to be withdrawn from a stream containing paraffins (branched and linear), branched olefins and aromatics. This can be done by separating the branched from the linear hydrocarbons, to improve yields and recoveries in the main step: complexation of olefins in a mixture with paraffins.

Separating branched from linear hydrocarbons can be done in two ways:

Simulated Moving Bed operation [2,3]

(+) Use of zeolites in a continuous way
(+) High recovery and purity in branched/unbranched hydrocarbons
(+) Proven industrial success (Molex, Olex)
(-) Need of a desorbent
(-) Complicated construction (because of alternating feed and withdrawal points in the column)
(-) Difficult to model
(-) Expensive (estimated at 120 million $ of total capital investment)

Zeolitic membrane [4,5,6]

(+) Use of zeolites in a continuous way
(+) High recovery and purity in branched/unbranched
(+) No need for a desorbent (separation based on diffusion in stead of adsorption)
(+) Simple and relatively cheap installation
(-) Sensitive ~~to solids~~ (~~clogging~~, rupture)
(-) Very low capacity because of low fluxes through the membrane (estimated membrane surface: five soccer fields).

There are many types of zeolites suitable for this separation [7], with relatively small differences in price and performance. Unfortunately both options are not suitable for our purposes. The first because of the costs, especially when put in perspective with our economical margin, the second because of the low capacity. This means that there can be no pre-treatment of the stream prior to complexation.

For complexation we have two alternatives:

Complexation through reaction with Cu(I)-salts [8,9,10]

- (+) Quick reactions
- (+) Easy separation from unreacted materials (solids)
- (-) Difficult regeneration
- (-) Environmental restrictions
- (-) Decreasing selectivity with increasing carbon number, starting at ethylene
- (-) Solid handling

Complexation through Diels-Alder reaction with anthracene [11,12,13]

- (+) High selectivities, also for C_5-C_8
- (+) High selectivity in branched over unbranched
- (+) Easy separation from unreacted materials
- (+) Easy regeneration
- (+) Easy separation after regeneration
- (-) Environmental restrictions
- (-) Slower complexation in respect to Cu(I) salts

In spite of slightly slower reactions, complexation with anthracene is favored. Because the Diels-Alder reaction is an equilibrium reaction (first order in both reactants, second order overall), the best thing to do is to bring the anthracene stream in countercurrent contact with the olefins stream at a temperature at which the olefin stream is gaseous and the anthracene stream is liquid, e.g. somewhere between 240 and 280 ^{O}C (at a pressure of 13 bar). At each stage equilibrium is assumed and so we can achieve high recoveries. No catalyst is needed for this reaction. Assumptions on kinetics will be made on the basis of **[11,12,13]**. The olefins will be lumped into certain categories and each category will be given a certain k-value, e.g. C_i-α, C_i-internals, branched.

After this, the equilibrium has to be reversed, choosing appropriate conditions (high(er) temperature and low(er) pressure) and the olefins have to be separated from the anthracene (large difference in boiling points) by simple distillation. It is still not certain whether this can be done in one UnitOp or not.

The anthracene can be recycled and we now have a stream of pure olefins (α, internal and a negligible amount of branched).

2.1.3 Higher olefin production

To produce the required C_{10}-C_{16} α-olefins, in this reaction section we are going to make use of a combination of oligomerization, metathesis and isomerization. One industrial example of this process is the SHOP (Shell Higher Olefin Process) **[14,15]**. Based on this SHOP, three alternatives came up. They are called "adapted SHOP", "ethylene oligomerization" and "lower olefins oligomerization".

First the three different reactions are explained, after which the three alternative processes are discussed.

Reactions

- **Oligomerization**

Small and intermediate molecules are connected to each other to form large molecules. Ethylene oligomerization yields α-olefins in the range C_4-C_{40}. The length of the produced chain varies with the reaction time. The shorter the reaction time, the smaller the produced chain.

The catalyst used is $[PhC(NSiMe_3)_2]_2CrCl$ **[16]**. The kinetics are determined on basis of **[16]**, in which conversion and product distribution of ethylene are given. The kinetics of the whole feed range are assumed on the latter data.

- **Metathesis**

Two double bond molecules connect and disconnect with their double bonds. The two chains have now swapped their alkyl groups. So $R_1{=}R_2 + R_3{=}R_4 \Rightarrow R_1{=}R_3 + R_4{=}R_2$. Metathesis with ethylene yields α-olefins. The catalyst used is Re_2O_7-on-Al_2O_3 **[14, 17-23]**. The kinetics are mainly based on **[22]**. References **[16-22]** are used to extrapolate and adjust the different data and provide a good base for the necessary assumptions.

- **Isomerization**

In this case we mean double-bond isomerization. The double bond shifts in the molecule. For instance isomerization of 1-pentene yields a mixture of 1-pentene, 2-pentene and 3-pentene. The catalyst used will be one of $H_3PW_{12}O_{40}$ and $(NH_4)_3PW_{12}O_{40}$ **[24]**. For both catalysts data on reaction time, conversion and product distribution on C_6-C_8 are available. Again the known data will be used to determine the kinetics for the broader feed range.

Alternatives (3x)

- **Adapted SHOP (see figure 2.1)**

~~First the~~ feed with the C_3-C_9 recycle from the separator is isomerized and subjected to metathesis in one step. This yields a range of internal olefins (C_2-C_{16}). These are again ~~subjected~~ tot metathesis with the isomerized recycle from the bottom of the separator and the ethylene recycle. ~~The~~ latter is mixed with fresh ethylene. To get all the input reacted, the molar ratio olefins: ethylene has to be at least 1:8 and preferably 1:15. The so formed α-olefins (range C_2-C_{30}) are the feed of a separator which leads the ethylene over the top, the C_3-C_9 near the top, the product in the middle (C_{10}-C_{16}) and the heavy fractions over the bottom (C_{16}+).

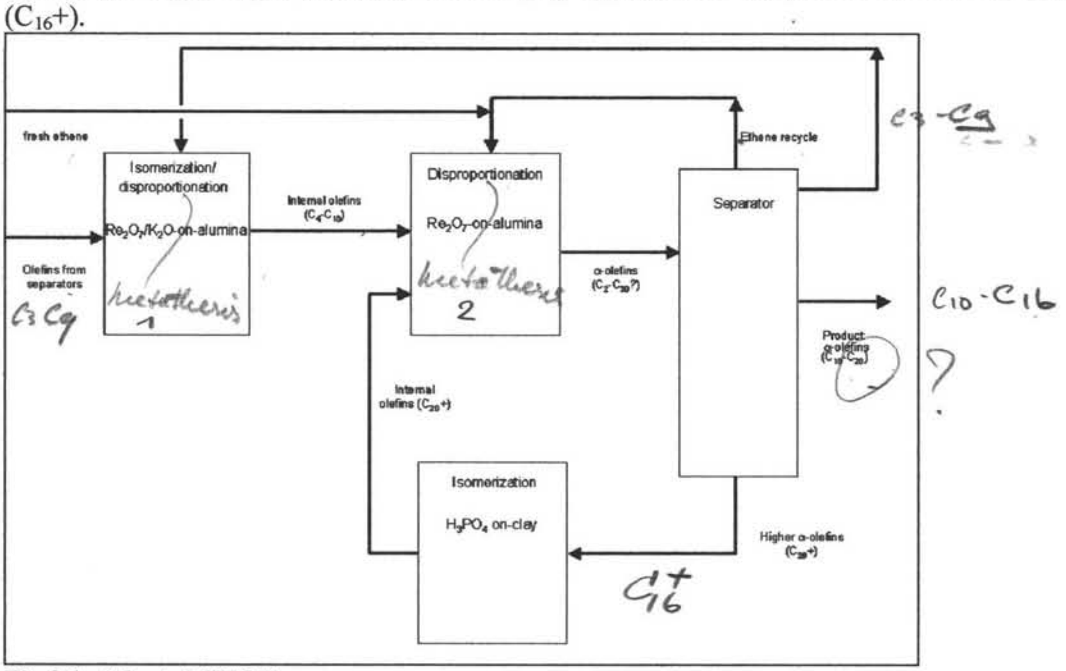

Fig 2.1: Adapted SHOP process

In general:

(+) Mainly α-olefins are produced
(-) Very low yield in required product
(-) Enormous recycles estimated 50 to 100 times the amount of feed
(-) Need of fresh ethylene

- **Ethylene oligomerization (figure 2.2)**

The feed is subjected tot metathesis, together with the isomerized recycled bottom product, the recycled oligomerized ethylene recycle and the C_2-C_9 recycle. The latter is again mixed with fresh ethylene. The product of the metathesis is the feed of the said separator.

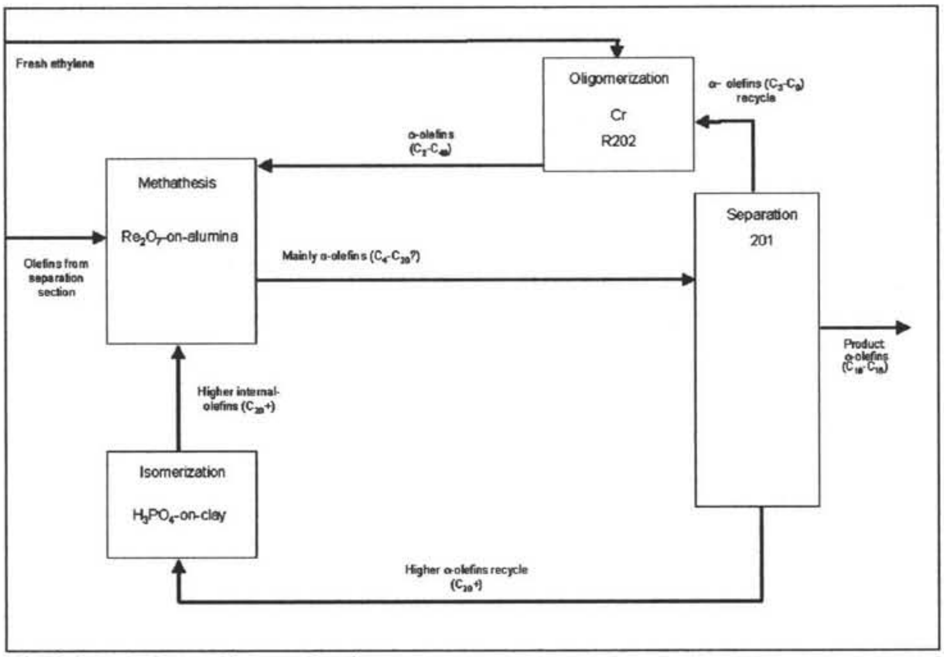

Fig 2.2: Ethylene oligomerization

In general:
(+) Mainly α-olefins are produced
(+) High yield in required product
(-) Olefin feedstock is only a small percentage of total feedstock
(-) Need of very large amounts of fresh ethylene

- **Lower olefins oligomerization**

The feed is first subjected to metathesis, together with the isomerized recycled bottom product and the ethylene recycle. The latter is again mixed with fresh ethylene. The product (C_4-C_{20} α-olefins) is oligomerized with the C_3-C_9 recycle to C_2-C_{54} α-olefins. The oligomerization product is separated in the said separator.

In general:
(+) High yield in required product
(+) Smallest possible recycles
(-) Need of fresh ethylene

The last possibility is the only one that yields an economically favorable amount of product with the olefin feedstock. The choice for the lower olefins separation is therefore the most logical.

2.2 Block schemes

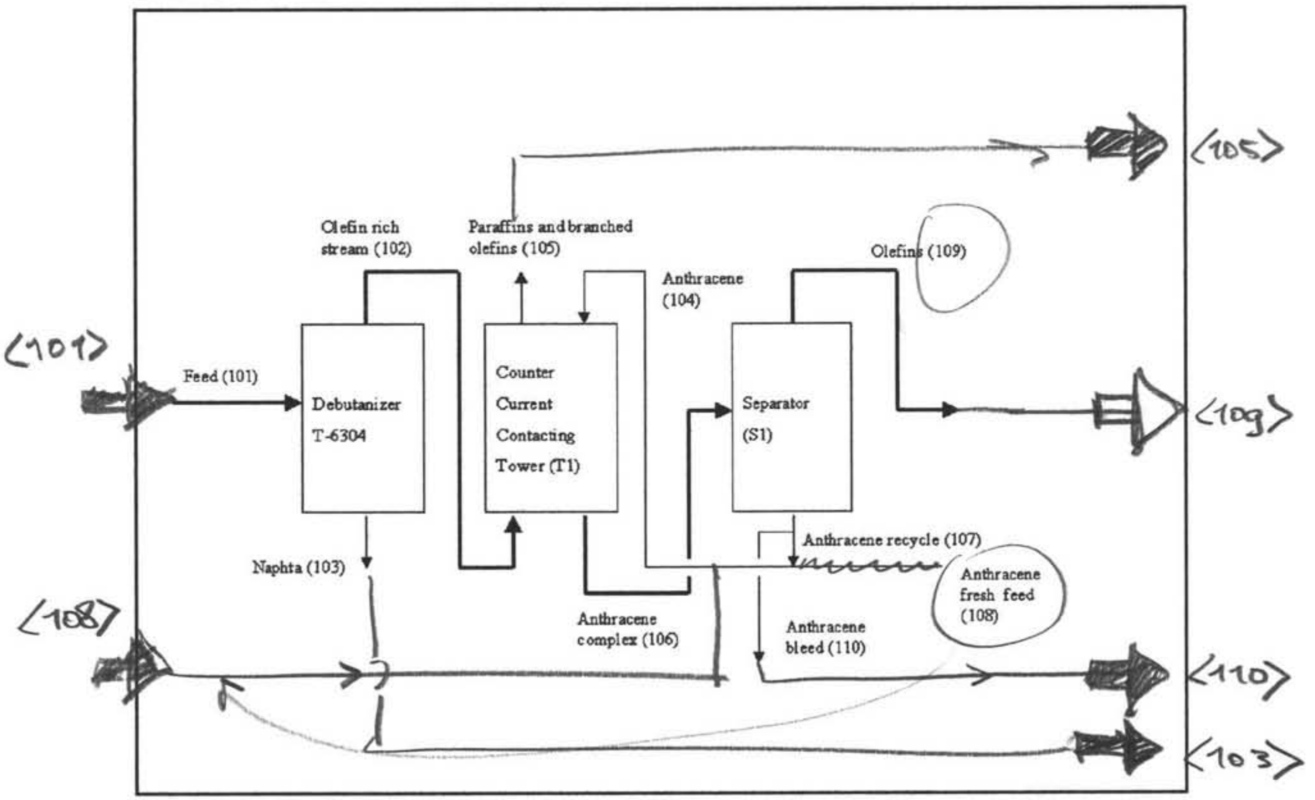

Fig. 2.3: Separation step

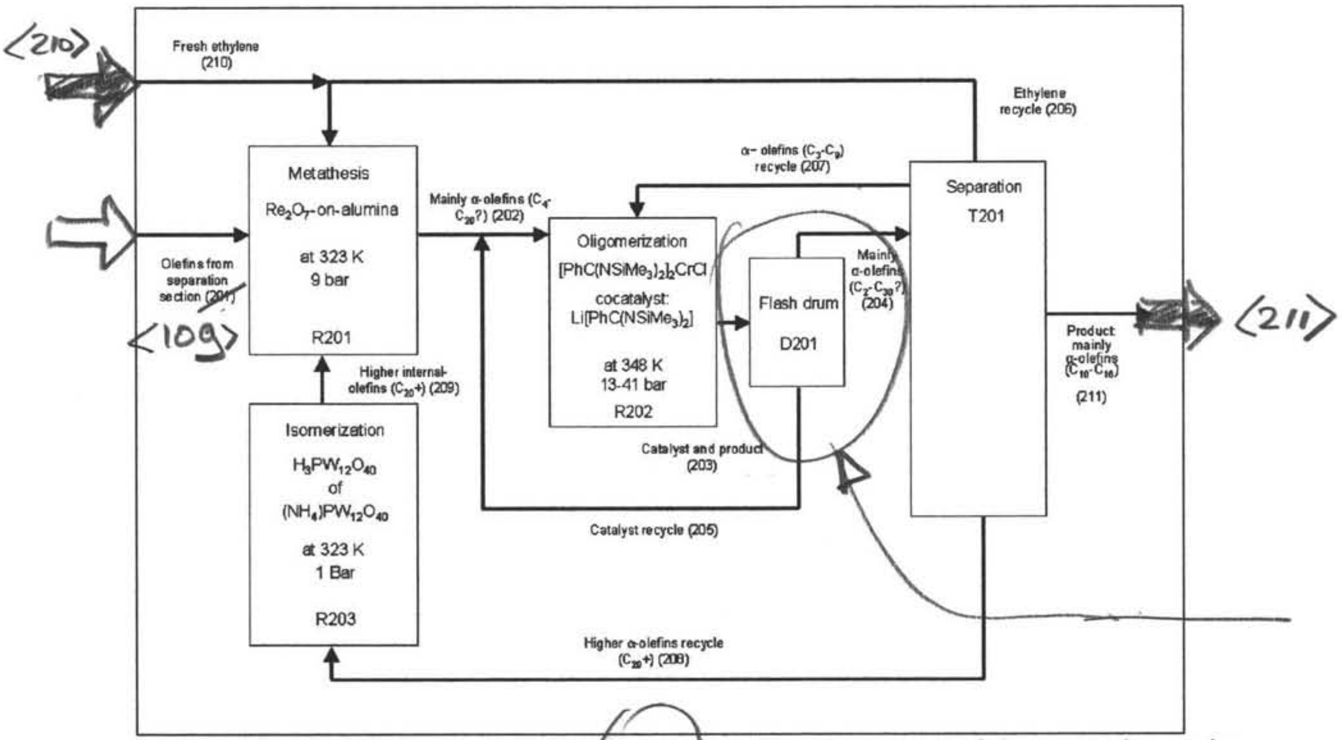

Fig. 2.4: Reaction step. The olefin stream 201 is the out-going stream of the separation section (stream 109)

2.3 Thermodynamic properties

The Peng-Robinson equation of state was determined to be the model to describe the thermodynamics of this process. This model is effective for predicting hydrocarbon systems at medium to high pressures. It is not necessary to use an activity coefficient method, because our components are not strongly non-ideal, or polar. Also, we are not dealing with polymers or electrolytes.

This method is suited best because accurate calculations for liquid densities are required, calculations are quick, and the model is capable of spanning a wide temperature range.

As an illustration, the x/y plots of two binary mixtures at moderate to high pressure simulated using the Peng-Robinson method are compared with literature data from the DECHEMA data series. The mixtures in question are ethane/n-butane and n-butane/n-hexane.

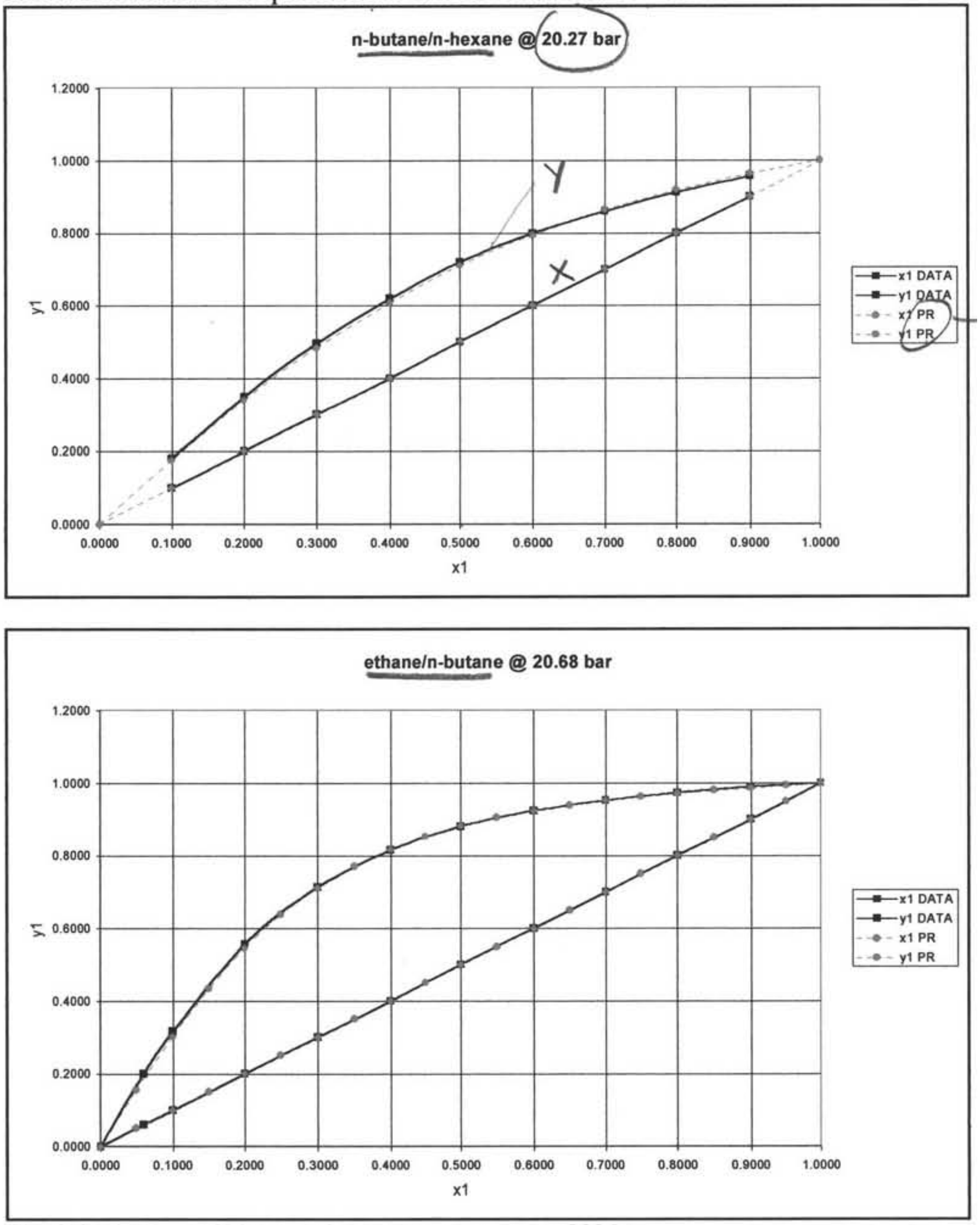

Fig. 2.4: x/y plots of binary mixtures at a pressure of 20 bar

2.4 List of pure component properties

Because of the large number of components present, only the lumped components will be given here. The given densities are relative to air or water, the components boiling at less than 0 °C relative to air, the components boiling above °C relative to water. oC °C

Table 2.1: Pure component properties MW BP MP Ref. Index

Component	Formula	M	Bp	Mp	Hazardous	Rel Den	Flamm	MAC
anthracene	$C_{14}H_{10}$	178	340	217,5		1,28		
ethane	C_2H_6	30,1	-89	-183		1,05	x	-
ethene	C_2H_4	28	-104	-169,2		0,98	x	-
10 propane	C_3H_8	44	-42	-187		1,60	x	-
propene	C_3H_6	42,1	-48	-185		1,50	x	500 ppm, 920 mg/l
I-butane	C_4H_{10}	58,1	-0,5	-138		2,01	x	600 ppm, 1430 mg/l
n-butane	C_4H_{10}	54,1	-5	-109		2,10	x	-
1,3-butadiene	C_4H_6	58,1	-12	-160	carcinogenic	1,90	x	21 ppm, 46 mg/l
1-butene	C_4H_8	56.1	-6	-185		1,90	x	-
vinyl acetylene	C_4H_4	52	2				x	
neopentane	C_5H_{12}	72,15	10	-17		0,59	x	
isopentane	C_5H_{12}	72,2	28	-160		0,60	x	-
1-pentene	C_5H_{10}	70,1	30	-165		0,60	x	-
n-pentane	C_5H_{12}	72,2	36	-130		0,60	x	600 ppm, 1800 mg/l
cyclopentene	C_5H_8	68,1	46	-93		0,77	x	-
10 cyclopentane	C_5H_{10}	70,1	49	-94		0,75	x	600 ppm, 1720 mg/l
1-hexene	C_6H_{12}	84,2	63	-140		0,70	x	
t-hexene-2	C_6H_{12}	84,2	68	-20		0,68	x	
n-hexane	C_6H_{14}	86,2	69	-95	nerve system	0,66	x	25 ppm, 90 mg/l
1,3-cyclohexadiene	C_6H_8	80,13	80	-98		0,86	x	
2,2,3-trimethylbutane	C_7H_{16}	100,2	81	-25		0,69	x	
cyclohexene	C_6H_{10}	82,14	83	-104		0,81	x	300 ppm, 1015 mg/l
3,3-dimethylpentane	C_7H_{16}	100,2	86	-134		0,69	x	
3-methylhexane	C_7H_{16}	100,2	92	-119		0,69	x	
n-heptane	C_7H_{16}	100,2	98	-91		0,68	x	300 ppm, 1200 mg/l
10 c-heptene-2	C_7H_{14}	98,2	98			0,71	x	
Toluene	C_7H_8	92,1	111	-95	nerve system	0,90	x	40 ppm, 150 mg/l
2,3,3-trimethylpentane	C_8H_{16}	114,2	99,2	-107		0,69	x	
t-octene-4	C_8H_{16}	112,2	122	-94		0,70	x	
2,2,4-trimethylhexane	C_9H_{20}	128,26	127	-120		0,72	x	
4-methyloctane	C_9H_{20}	128,26	142	-113		0,72	x	
o-xylene	C_8H_{10}	106,2	144	-25	nerve system	0,90	x	50 ppm, 210 mg/l
n-hexylmercaptan	$C_6H_{14}S$	118,2	152	-80		0,82		
1-methyl-4-ethylbenzene	C_9H_{12}	120,2	162	-62		0,86		
5-methylnonane	$C_{10}H_{22}$	142,3	165	-88		0,73		
n-decane	$C_{10}H_{20}$	142,3	174,1	-29,7		0,73		
10 4-ethyl-o-xylene	$C_{10}H_{14}$	134,2	190	-67		0,88		
1,2,3,4-tetrahydronaphthalene	$C_{10}H_{12}$	132,2	207	-35		0,97		
n-dodecane	$C_{12}H_{26}$	170,3	216,3	-9,6		0,75		
naphthalene	$C_{10}H_8$	128,2	218	80,6		1,00		

$\Sigma = 30$

The complexes between anthracene and olefins, used in the separation step, can not be found in any handbook. However, only few properties are of interest to us, and most properties can be estimated using anthracene as a basis or can be modeled in Insight II (a molecular modeling program).

Table 2.2: Pure component properties of the complexes

Stof	Formula	M	Bp (1)	Mp (1)	Schadelijk	DHf (2)	Cp (3)	
3-A	$C_{17}H_{16}$	220	360	240	Similar to anthracene		1,8	1. Estimate based on anthracene
4-A	$C_{18}H_{18}$	234	390	250	Similar to anthracene		1,8	and the olefin in question
5-A	$C_{19}H_{20}$	248	420	260	Similar to anthracene		1,8	2. Will be modeled in Insight II
6-A	$C_{20}H_{22}$	262	450	270	Similar to anthracene		1,8	3. 90% of the value for anthracene

The same properties will be assumed for the isomers of these olefins, except for the heat of formation which will be higher for the 2-branched adduct compared to the linear adduct.

2.5 Process stream summary and mass balances

In this design, especially in the separation, the lumping of components makes it difficult to make a straightforward mass balance of the process. Lumping takes place first on basis of boiling point (in the debutanizer) and then on basis of chemical properties (in the complexation with anthracene). Furthermore the complexity of the stream makes balancing the stream a time-consuming task.

The mass balance presented here is a balance of the streams crossing the battery limits.

Table 2.3: Process stream summary

PROCESS STREAM SUMMARY					
STREAM Nr.:		101 IN	108 IN	207 IN	
Name:		Feed T-6304	Anthracene	Ethylene	
		ton/h	ton/h	ton/h	
Total		153	2	24	
Phase		V	L	V	
Pressure	Bar g	21	13	9	
Temp	°C	170	250	50	

STREAM Nr.:		103 OUT	105 OUT	110 OUT	209 OUT
Name:		T-6304 bottom	Paraffin extract	Bleed complex	Product
		ton/h	ton/h	ton/h	ton/h
Total		94	35	2	48
Phase		L	V	L	L
Pressure	Bar g	13	13	13	1
Temp	°C	270	250	250	25

Overall Mass balance					
STREAM Nr.:		101+108+207 IN	103+105+110+209 OUT	OUT-IN	
Name:		Total Plant	Total Plant	Total Plant	
		ton/h	ton/h	ton/h	
Total		179	179	0	
Pressure	Bar g				
Temp	°C				

$C_2^=$
0.5 t/t prod

3. Basic Assumptions

3.1 Feedstocks

3.1.1 Feed T-6304

The coker naphtha will be provided from the Flexicoking unit. The design specifications differ from the real specifications, because all the components are lumped with representatives. This is done by boiling point to achieve a good ASTM curve (see Appendix A). For example, branched c5 olefins are lumped with the c5 alpha olefin representative. After the debutanizer (T-6304), the components will be de-lumped again into a satisfactory set of components for the olefin/paraffin separation step.

Table 3.1: Composition of the feed stream

Stream name:			Feed T-6304		
Comp.	*Units*	*Specification*		*Notes*	*Additional information*
		Available	Design		
alpha olefins	***%wt***	12,50	15,1	(1)	(1) Values taken because of lumping for appropriate boiling point curve
internal olefins	***%wt***	6,50	10,6	(2)	
branched olefins	***%wt***	14,50	0,0	(2)	
cyclic olefins	***%wt***	1,00	7,1	(2)	(2) Branched olefins lumped with alpha, internal and cyclic olefins
paraffins	***%wt***	34,80	38,8	(1)	
benzenes	***%wt***	15,00	8,6	(1)	
heavy end	***%wt***	15,00	19,1	(1)	
sulphur	***%wt***	0,7000	0,6000		
nitrogen	***%wt***	0,0150	0,0130		
Total		100,0	100,0		
Process conditions and price					
Temperature	**°C**	170,0			
Pressure	**Bar g**	21,0			
Phase	**V/L/S**	V/L			
Price	**$/ton**	150,0			

3.1.2 Anthracene

Table 3.2: Composition of the anthracene

Stream name:			Anthracene		
Comp.	*Units*	*Specification*		*Notes*	*Additional information*
		Available	Design		
Anthracene	***%wt***	95,00			
Other	***%wt***	5,00			
Total		100,0	0,0		
Process conditions and price					
Temperature	**°C**	250,0			
Pressure	**Bar g**	13,0			
Phase	**V/L/S**	L			
Price	**$/ton**	2000,00			

3.1.3 Chemical grade ethylene

The ethylene will be provided by pipeline from outside the Esso plant. However ethylene and the necessary installations for the transport thereof are very expensive (2.5 million $), the process requires ethylene to convert the internal olefins into alpha olefins.

Table 3.3: Composition of the chemical grade ethylene

Stream name:				*chemical grade ethylene*	
Comp.	*Units*	*Specification*		*Notes*	*Additional information*
		Available	Design		
Ethene	***%wt***	?	99,0		
Other	***%wt***	?	1,0		
Total		0,0	100,0		
	Process conditions and price				
Temperature	**°C**	?			
Pressure	**Bar g**	?			
Phase	**V/L/S**	V			
Price	**$/ton**	500,00			

3.2 Products

3.2.1 Alpha olefin product

The product will be consisting mainly of alpha olefins suited for use in detergents (c10-c16 range).

Table 3.4: The alpha olefin product composition

Stream name:				*Alpha olefins*	
Comp.	*Units*	*Specification*		*Notes*	*Additional information*
		Available	Design		
<C10 alpha	***%wt***	5,00			(1) These include mainly internal olefins
C10-C16 alpha	***%wt***	80,00			
>C16 alpha	***%wt***	5,00			
Other	***%wt***	10,00		(1)	
Total		100,0	0,0		
	Process conditions and price				
Temperature	**°C**	20,0			
Pressure	**Bar g**	1,0			
Phase	**V/L/S**	L			
Price	**$/ton**	1750,00			

3.2.2 Bottom product T-6304

The bottom product of the debutanizer will contain more heavy fraction than it does in the present situation. This may affect its current use as lean oil in the deethanizer.

Table 3.5: The composition of the T-6304 bottom

Stream name:			Bottom T-6304	
Comp.	Units	Specification	Notes	Additional information
		Design		(1) All N and S exit through the bottom of T-6304
alpha olefins	*%wt*	0,0		
internal olefins	*%wt*	10,0		
branched olefins	*%wt*	0,0		
cyclic olefins	*%wt*	2,0		
paraffins	*%wt*	35,0		
benzenes	*%wt*	35,0		
heavy end	*%wt*	16,9		
sulphur	*%wt*	1,0	(1)	
nitrogen	*%wt*	0,1	(1)	
Total		100,0		
Process conditions and price				
Temperature	°C	270,0		
Pressure	Bar g	13,0		
Phase	V/L/S	L		
Price	$/ton	125,0		

3.2.3 Paraffin extract

The top stream from the debutanizer is led to the anthracene contacting tower. The paraffins are extracted from the olefin rich stream in this tower. The composition of the extract will be:

Table 3.6: The composition of the paraffin extract

Stream name:				paraffin extract	
Comp.	Units	Specification		Notes	Additional information
			Design		(1) 90 % of the branched olefins won't react with antracene
branched olefins	*%wt*		20,0	(1)	
paraffins	*%wt*		80,0	(2)	(2) all paraffins exit with this separation
Total		0,0	100,0		
Process conditions and price					
Temperature	°C	200,0			
Pressure	Bar g	13,0			
Phase	V/L/S	V			
Price	$/ton	125,00			

3.3 Plant capacity

The plant is located in Pernis, near Rotterdam, as it is a downstream add-on to the Flexicoking process already present there. The battery limits are considered to be the two block schemes in chapter 2.2. Anything else is considered as environment. The environment will provide us with anthracene and ethylene, necessary in respectively the separation and reaction.

3.4 Catalyst Specifications

At three stages in the reaction section catalysts are used: In the metathesis, the oligomerization and the isomerization.

The metathesis uses Re_2O_7 on alumina as a heterogeneous catalyst. In reference **[22]** typical catalyst/feed ratios are mentioned in the range of 10-20 mol kg Cat.$^{-1}$ s^{-1}. When we assume a feed to the metathesis step of 100 ton/h, the necessary amount of active catalyst is about 20 kg.

In the oligomerization section a catalyst and co-catalyst are used, being $PhC(NSiMe_3)_2]_2CrCl$ and $Li[PhC(LiNSiMe_3)_2]$. In the data of reference **[16]** an activity of 982.3 kg α-olefins/ kg chromium cat/hour is found, based on this activity and a process product stream of 48 tons per hour and the fact that only 35 % of the oligomerization product consists of α-olefins in the product range the oligomerization reactor would need 147 kg catalyst and the equal amount of co-catalyst. Because the oligomerization is a homogeneous catalyzed process a separation step is needed to recover the catalyst and prevent it from entering the product stream and the recycles. For this purpose the stream is flashed and the liquid phase, containing the catalyst, is recycled to the oligomerization reactor. Because of this recycle the needed amount of
(co-)catalyst will be greater than the amount needed in the reactor.

The isomerization uses either $H_3PW_{12}O_{40}$ or $(NH_4)_3PW_{12}O_{40}$ as the heterogeneous catalyst. In the data of reference **[24]** the catalyst/olefin ratio used is 1 g cat / 10 ml . This is approximately 8 gram olefin per gram catalyst. The estimated feed stream to the isomerisation reactor is 50 ton/h, so the needed catalyst amount is 6 ton.

Table 3.7: Catalyst properties

Catalyst	*Reaction*	*Homo/Heterogeneous*	*Amount [kg]*
Re_2O_7 on alumina	Metathesis	Heterogeneous	20
$PhC(NSiMe_3)_2]_2CrCl$ and $Li[PhC(LiNSiMe_3)_2]$	Oligomerization	Homogeneous	150
$H_3PW_{12}O_{40}$	Isomerization	Heterogeneous	6000

4. Economic potential

To calculate the economic margin within which the design must be realized, we simply subtract the value of the ingoing streams from the product stream.

Table 4.1: Prices of materials

Material	*Stream ID*	*Price*	*Unit*	*Source*
LPG stream	102	200	$/ton	Given by J. de Glopper
Naphtha stream	103	125	$/ton	Given by J. de Glopper
Anthracene	108	2000	$/ton	Estimate
Ethylene	207	450	$/ton	Given by J. de Glopper
Olefins after separation	109	1250	$/ton	Given by J. de Glopper
Detergent intermediates	209	1750	$/ton	PEP yearbook

As stated in chapter 1 we will evaluate the process after separation and after reaction. Because the ingoing stream of the debutanizer has no economical value, the margin will be calculated using the product stream of the debutanizer, before and after changing the operating conditions. The lean oil stream, which is split from the bottom stream of the debutanizer, is excluded.

Table 4.2: Economical margin for separation (left) and reaction (right)

Stream ID	*Amount (tons/hr.)*	*Value ($/hr.)*	*Stream ID*	*Amount (tons/hr.)*	*Value ($/hr.)*
102 (LPG)	19	3800 (-)	*201*	24	30000
103 (Naphtha)	54	6750 (-)	*207*	24	12000
103+105	46	5750 (+)	*209*	48	84000
108	2	4000 (-)			
109	24	30000 (+)			
Revenue per hour		21200	*Revenue per hour*		42000
Revenue per annum		173.2 million	*Revenue per annum*		343.1 million

Now, to calculate the maximum capital investment we use a Discounted Cash Flow Rate of Return (DCFROR) of 35% for the separation, 60% for the reaction (both demanded by Exxon) and an average plant life of ten years.
When we calculate the results we come to an allowed total capital investment of 415 million $.

Table 4.3: Total revenues for separation

Year	*Revenue (in million $)*	*Discounting Factor*	*PV (in million $)*	*Plant Capacity*
		0,35		
1	104	0,741	77	0,6
2	156	0,549	85	0,9
3	164	0,406	67	0,95
4	173	0,301	52	1
5	173	0,223	39	1
6	173	0,165	29	1
7	173	0,122	21	1
8	173	0,091	16	1
9	173	0,067	12	1
10	173	0,050	9	1
	Working capital		10	
	Salvage		--	
	PV return		**415**	
	Yearly revenue		173	

For the reaction we have larger yearly revenues and so our total capital investment comes to 473 million $, if we want to break-even.

Table 4.4: Total revenues for reaction

Year	*Revenue (in million $)*	*Discounting Factor*	*PV (in million $)*	*Plant Capacity*
		0,6		
1	206	0,625	129	0,6
2	309	0,391	121	0,9
3	326	0,244	80	0,95
4	343	0,153	52	1
5	343	0,095	33	1
6	343	0,060	20	1
7	343	0,037	13	1
8	343	0,023	8	1
9	343	0,015	5	1
10	343	0,009	3	1
	Working capital		10	
	Salvage		--	
	PV return		**473**	
	Yearly revenue		343	

So for the complete process we come to a maximum total capital investment of 988 million $.
These calculations are made under the assumption that working capital is about 10 million $ (containing a month's supply of feedstock plus some extra expenses like storage and salaries) and there is no salvage value at the end of the plant's life.
If we use the raw estimate that Total Capital Investment ≈ 2.36 Onsite **[25]**, we can conclude that we can spend a maximum of 419 million $ for installation hardware.

5. Literature

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Appendix A: Lumping components and ASTM curve of the coker naphtha

Table A.1: Lumped components representing the coker naphtha

component	%w	Bp (°C)
1-butene	0,13	-6
vinyl acetylene	2,20	2
neopentane	1,57	10
isopentane	0,60	28
1-pentene	3,64	30
n-pentane	2,38	36
cyclopentene	5,30	46
cyclopentane	0,46	49
1-hexene	5,72	63
t-hexene-2	1,97	68
n-hexane	2,15	69
1,3-cyclohexadiene	0,33	80
2,2,3-trimethylbutane	1,56	81
cyclohexene	2,63	83
3,3-dimethylpentane	1,36	86
3-methylhexane	3,22	92
n-heptane	3,63	98
c-heptene-2	3,28	98
2,3,3-trimethylpentane	2,08	99
Toluene	0,41	111
t-octene-4	4,48	122
2,2,4-trimethylhexane	5,59	127
4-methyloctane	3,16	142
o-xylene	4,10	144
n-hexylmercaptan	2,56	152
1-methyl-4-ethylbenzene	2,50	162
5-methylnonane	2,32	165
n-decane	1,65	174
4-ethyl-o-xylene	2,94	190
1,2,3,4-tetrahydronaphthalene	3,69	207
n-dodecane	11,32	216
naphthalene	5,30	218
n-decylamine	0,17	221
n-hexylbenzene	4,00	226
1-methylnaphthalene	1,60	240

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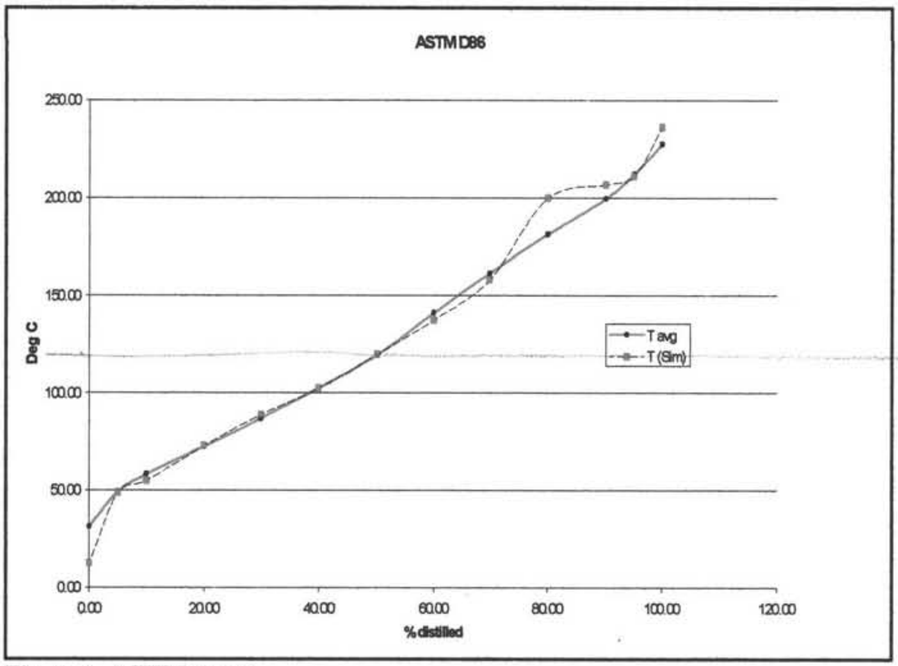

Fig. A.1: ASTM curve

The simulated ASTM curve is compared with the ASTM data of the coker naphtha provided by Esso. The light ends are well described by the representatives of the components. Since the light ends (C3-C8) are the most important components in the naphtha and the heavy ends leave the debutanizer in our design, this set of components should be good enough to describe all our components.