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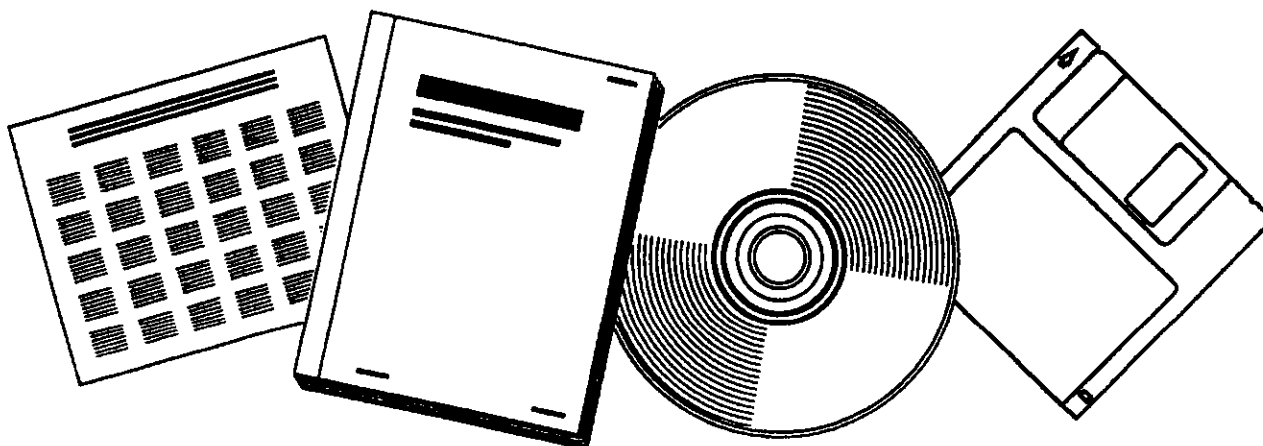
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# SELECTIVITY IN FISCHER-TROPSCH SYNTHESIS: REVIEW AND RECOMMENDATIONS FOR FURTHER WORK

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL  
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CHEMICAL ENGINEERING GROUP

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REVIEW AND RECOMMENDATIONS FOR FURTHER WORK

**L. CALDWELL**

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SOUTH AFRICA

S Y N O P S I S

A broad product spectrum is obtained from the Fischer-Tropsch synthesis aimed at the production of gasoline and diesel fuels. This is a consequence of the carbon atom by carbon atom mechanism of chain growth. There is potential for narrowing the product spectrum by use of dual-function catalysts or transient process conditions.

SELEKTIWITEIT IN DIE FISCHER-TROPSCH SINTESE

Oorsig en aanbevelings vir verdere werk

S I N O P S I S

Uit die Fischer-Tropsch sintese, wat gemik is op die vervaardiging van petrol en dieselolie, word 'n breë spektrum van produkte verkry. Dit is 'n gevolg van die meganisme van die groei van die koolstofketens wat steeds met een koolstofatoom toeneem. Dit lyk egter moontlik om die produkspektrum te vernou deur gebruikmaking van 'n katalisator met meer as een funksie of van wisselende prosesondisies.

KEYWORDS: Fischer-Tropsch, carbon monoxide hydrogenation, selectivity, review

File No: 660-50-2

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## 1 INTRODUCTION

The catalytic hydrogenation of carbon monoxide to produce paraffins and olefins (together with some oxygenated compounds) is known as the Fischer-Tropsch synthesis. The generalised reaction scheme for paraffin production may be written



where  $n$  can, according to the conditions, take any value from unity to several thousand.

The commercial significance of this reaction is that it provides a route for the production of liquid fuels from coal via gasification to carbon monoxide and hydrogen. Pioneering research by Fischer, Tropsch, Pichler and others<sup>(1)</sup> in the period 1925 – 1942 led to the construction of industrial plants in Germany during the Second World War which made an important contribution to that country's gasoline and diesel fuel requirements. Interest in the reaction flagged after the War, apart from the construction of the Sasol plant in South Africa and an abortive attempt to operate a fluidised-bed process in the United States<sup>(2)</sup>, because liquid fuels were plentiful and cheap. Today, however, with the prospect of oil supplies drying up completely in the foreseeable future, whilst coal remains relatively abundant, there is a great revival of interest in Fischer-Tropsch studies<sup>(3,4)</sup>.

It is not intended here to provide a comprehensive review of the subject<sup>(4,5)</sup>, but to discuss the literature dealing with reaction selectivity for gasoline and diesel fuels, and to make recommendations for the direction of future research in this area.

## 2 SELECTIVITY AND MECHANISM

The generalised reaction scheme for saturated hydrocarbon production in a Fischer-Tropsch reactor has been given above. It is a well-known feature of the reaction that the product distribution cannot be closely controlled<sup>(5,6,7)</sup>; in other words, one cannot obtain a hydrocarbon product in which the individual molecules all have exactly  $n$  carbon atoms, nor even a product where  $n$  is constrained in some narrow range,  $a \leq n \leq b$ . The exception to this rule is the so-called methanation reaction in which methane is the sole product. According to some views methanation is distinct from the Fischer-Tropsch reaction; other authors regard it as simply the first stage<sup>(4,8)</sup>.

TABLE 1 Product distribution for the Sasol I reactors<sup>(9)</sup>  
(Figures in mass %)

CARBON NUMBER	1	2-4	5-12	13-18	19-21	22-30	>30	Oxygenates etcetera
Fixed bed	5,0	12,6	22,5	15,0	6,0	17,0	18,0	3,9
Transported bed	10,0	33,0	39,0	5,0	1,0	3,0	2,0	7,0

Table 1 shows the distribution of products obtained in the Sasol fixed and transported-bed reactors under typical operating conditions<sup>(9)</sup>. It is obvious that the process leaves much to be desired if gasoline ( $C_5 - C_{12}$ ) and diesel oil ( $C_{13} - C_{18}$ ) are the required end products.

Factors influencing selectivity are discussed below.

## 2.1 CHOICE OF CATALYST

The "traditional" catalysts are iron, cobalt and nickel, of which iron and cobalt have been most favoured. Early German plants used cobalt, but considered switching to iron in 1943; the Hydrocol plant in the USA used an iron catalyst, as does the Sasol process in South Africa. Nickel is predominantly a methanation catalyst, cobalt gives mostly straight chain paraffins, whilst iron gives paraffins, olefins and oxygenated products<sup>(1,2,5)</sup>. Obviously the cost of the catalyst is a major consideration, and this gives iron an advantage over all others.

Enormous effort has been expended on studying the influence of promoters and carriers on catalyst performance<sup>(1,5)</sup>. Although much has been learned and it is to some extent possible to "tailor" a catalyst to produce a given range of products (in conjunction with the proper choice of operating conditions), the basic problem of obtaining selectivity for a narrow range still remains.

Other catalysts which have been tried comprise the rest of the Group VIII metals and a number of metal oxides. Pichler showed that ruthenium was an excellent catalyst at low temperatures and high pressures for the production of very high molecular weight paraffins<sup>(10,11)</sup>. Table 2 shows the product spectra reported by him for a typical experiment.

**TABLE 2**      Product distribution on a ruthenium oxide catalyst suspended  
in n-nonane at 405 K and 1 000 bar<sup>(11)</sup>

<b>MEAN CARBON NUMBER OF FRACTION</b>	41,4	62,1	111,1	204	241	611	3 260	6 050
<b>MASS %</b>	14,0	16,3	5,3	11,7	11,9	13,4	18,0	9,4

More recently Anderson et al<sup>(12)</sup> showed that a 0,5% ruthenium on alumina catalyst at moderate pressures and temperatures gave a product distribution similar to that found with cobalt or iron. Zinc oxide and oxides in general have been found useful for the production of methanol and higher alcohols.

## 2.2 OPERATING CONDITIONS

The influence of temperature and pressure on the course of the reaction is straightforward. Increasing the temperature increases the rate of reaction but decreases the chain length of the products. Some recently published data of King are shown in Figure 1<sup>(13)</sup>. Other workers<sup>(5)</sup> report similar findings; Dry<sup>(6)</sup> indicates that the effect of temperature on selectivity is greater in reactors producing high molecular weight products than in reactors giving mainly light ends.

Increasing total pressure has in general the effect of increasing both the extent of conversion and the chain length of the products. This is illustrated by the data of Table 3 and Figure 2<sup>(1)</sup>, and is to be expected on thermodynamic grounds because of the contraction in volume which takes place upon reaction.



FIGURE 1 Effect of temperature on chain length<sup>(13)</sup>

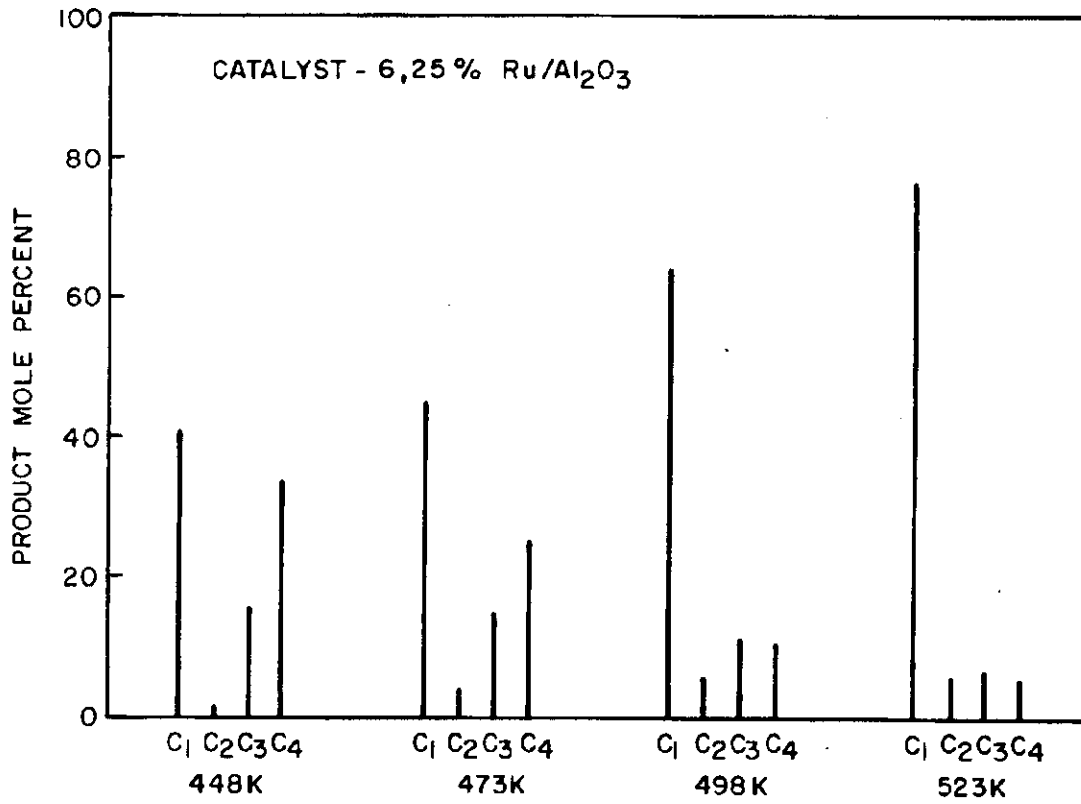
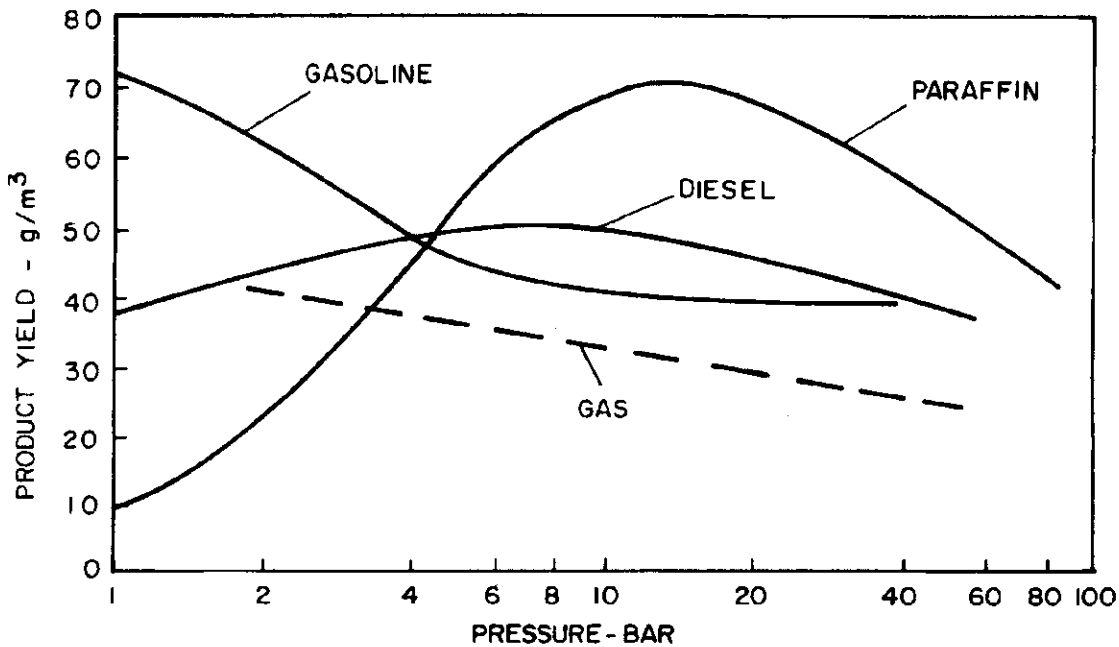


FIGURE 2 Effect of pressure on chain length<sup>(1)</sup>



**TABLE 3**      Effect of total pressure on conversion and  
product chain length for a ruthenium catalyst at 453 K<sup>(1)</sup>

Pressure Bar	CO Conversion %	% Converted CO to		
		Paraffin Wax	Liquid Hydrocarbons	Gaseous Hydrocarbons
1	0	—	—	—
51	48	46	33	21
101	68	53	31	16
1 013	92	59	26	15

As Figure 2 indicates, however, the effect on a particular range of products may be quite small for pressure changes of several bar, and this has been confirmed by Everson et al<sup>(14)</sup> working with a ruthenium catalyst between 8 and 16 bar. Figure 2 also shows that beyond a certain point the yield of all products begins to fall off with further increase of pressure. This has been attributed to carbonyl formation, but may also be due to the blocking of the catalyst surface by high molecular weight products.

The ratio of hydrogen to carbon monoxide in the reaction mixture has a pronounced effect on selectivity (as well as on reaction rate), at least in the case of fixed-bed reactors. Figure 3 shows data of Anderson et al<sup>(12)</sup> obtained with a ruthenium catalyst for H<sub>2</sub>:CO(CO<sub>2</sub>) ratios from 1:1 to 4:1. At a ratio of 4:1 the conversion reached 80% and the product was almost pure methane; at a 1:1 ratio the conversion was only 40% but products were obtained from methane up to waxes boiling in excess of 737 K. Dry<sup>(15)</sup> reports similar findings for a fixed-bed reactor, but states that the H<sub>2</sub>:CO ratio is of no importance in determining selectivities in fluidised-bed operation; all the results reported by him for fluidised beds were for H<sub>2</sub>:CO ratios in excess of 3:1.

FIGURE 3 Effect of feed gas composition on product distribution<sup>(12)</sup>

$4\text{H}_2 + 1\text{CO}_2$	$3\text{H}_2 + 1\text{CO}$	$2\text{H}_2 + 1\text{CO}$	$1\text{H}_2 + 1\text{CO}$	Gas Composition		
82	77	66	40	Conversion %		
$\text{C}_1$	$\text{C}_1$	$\text{C}_1$	$\text{C}_1$	Distribution of hydrocarbons, percent by mass		
		$\text{C}_2 - \text{C}_4$	$\text{C}_2 - \text{C}_4$		90	
		$< 458 \text{ K}$	$< 458 \text{ K}$		80	
		$< 458 \text{ K}$	$< 458 \text{ K}$		70	
	$\text{C}_2 - \text{C}_4$	$458 - 625 \text{ K}$	$458 - 625 \text{ K}$		$458 - 625 \text{ K}$	60
			$458 - 625 \text{ K}$		$458 - 625 \text{ K}$	50
	$< 458 \text{ K}$	$625 - 737 \text{ K}$	$625 - 737 \text{ K}$		$625 - 737 \text{ K}$	40
			$625 - 737 \text{ K}$		$625 - 737 \text{ K}$	30
	$458 - 625 \text{ K}$	$> 737 \text{ K}$	$> 737 \text{ K}$		$> 737 \text{ K}$	20
			$> 737 \text{ K}$		$> 737 \text{ K}$	10
$\text{C}_2 - \text{C}_4$				0		

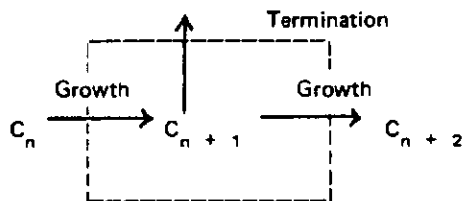
The influence of space velocity on selectivity has not been studied extensively. It is difficult to isolate the effect of this variable, since inevitably conversions decrease with increasing space velocity and hence the partial pressure of reactants will also vary. Dry<sup>(15)</sup>, working with an iron catalyst in a differential reactor, showed that the productivity (i.e. the total amount of CO and  $\text{H}_2$  reacted) did not change over a ninefold variation in space velocity. The  $\text{CO}_2:\text{H}_2$  ratio was, however, greater at low space velocity which indicates that  $\text{CO}_2$  is a product of secondary (water gas shift) reaction. Dry did not report variations in the hydrocarbon product. Pichler, Schulz and other workers<sup>(16,13)</sup> have shown that the  $\alpha$ -olefin content of the product increases with increasing space velocity, indicating that  $\alpha$ -olefins are primary products. This view is supported by the fact that  $^{14}\text{C}$  containing olefins added to the synthesis gas can be incorporated into the Fischer-Tropsch product<sup>(17)</sup>.

### 2.3 MECHANISM

The detailed mechanism of the Fischer-Tropsch reaction has been and remains a subject of controversy<sup>(4,8,18)</sup>. Despite this there is a measure of agreement amongst research workers as to what takes place on the catalyst surface, and this common ground is sufficient to provide a model which can be verified by the bulk of the experimental evidence. It is the opinion of the writer that improvements to the Fischer-Tropsch process are more likely to derive from a consideration of this model and its implications than from an examination of the fine detail of the chemical mechanism.

The assumptions of the model can be simply stated:

1. Reaction is initiated on the surface by some species containing a single carbon atom.
2. Chain growth takes place from the initiating species by the *addition of one carbon atom at a time*.
3. Chain growth is terminated in some way which leads to desorption of the product molecule and creates a vacant site on the surface for further reaction.
4. The rates of the growth and termination reactions are independent of the chain length, and are of the *same order* in the surface concentration of the species in question.



- Let  $N_n$  = Number of surface sites occupied by chains of length  $n$ .  
 $K_1$  = Rate constant for growth reaction (independent of  $n$ ).  
 $K_2$  = Rate constant for termination reaction (independent of  $n$ ).

Under steady-state conditions the surface concentrations of all species are constant and hence

Rate of growth of  $n$ th species

$$= \text{Rate of growth} + \text{Rate of termination of } (n + 1)\text{th species.}$$

$$\therefore K_1 f_1 N_n^x = K_1 f_1 N_{n+1}^x + K_2 f_2 N_{n+1}^x$$

where  $x$  is the reaction order and  $f_1, f_2$  indicate the dependence of the growth and termination reactions on the hydrogen and carbon monoxide activities.

$$\therefore \left[ \frac{N_{n+1}}{N_n} \right]^x = \frac{K_1 f_1}{K_1 f_1 + K_2 f_2} = \frac{1}{1 + Kf}$$

$$\text{where } K = \frac{K_2}{K_1}, \quad f = \frac{f_2}{f_1}$$

If reaction conditions are constant then

$$\left[ \frac{1}{1 + Kf} \right]^{1/x} = a \quad (\text{a constant})$$

and

$$N_{n+1} = a N_n \quad (1)$$

Hence also

$$N_n = a^{n-1} N_1$$

and

$$\begin{aligned} \sum_1^n N_n &= N_1 (1 + a + a^2 + \dots + a^{n-1}) \\ &= N_1 \left[ \frac{1 - a^n}{1 - a} \right] \end{aligned}$$

Hence the total number of occupied sites on the surface is given by

$$\sum_1^\infty N_n = N_1 \left[ \frac{1}{1 - a} \right]$$

since  $a < 1$  and  $a^n \rightarrow 0$  as  $n \rightarrow \infty$ .

The fraction of sites occupied by chains of length  $n$  is then

$$x_n = \frac{N_n}{\sum_1^\infty N_n} = (1 - a) a^{n-1} \quad (2)$$

Since the rate constant for desorption (termination) is independent of chain length it follows that the mole fractions of products in the gas phase (based on total product) will be the same as on the catalyst surface.

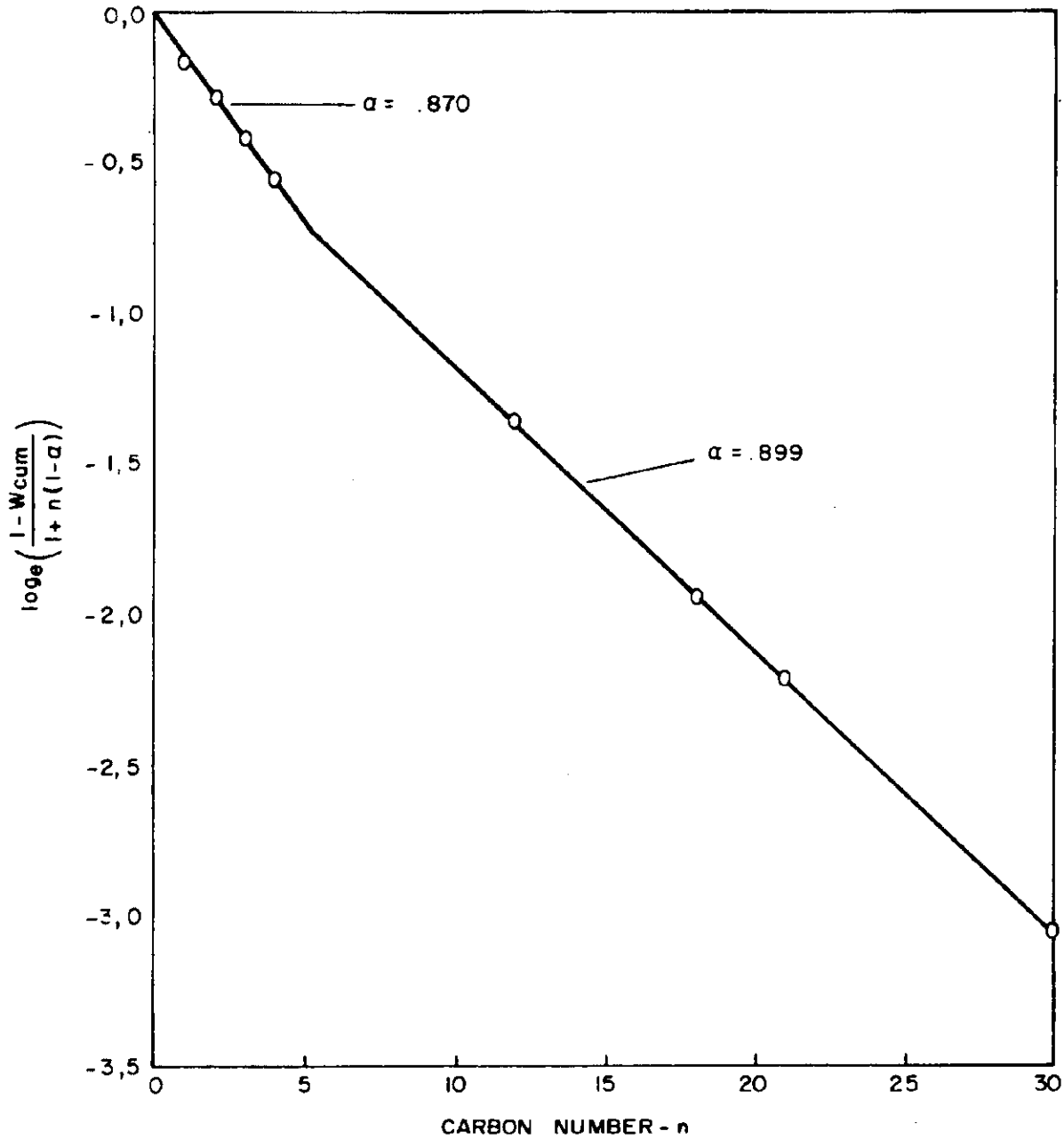
Equation (2) can be written as

$$\log(x_n) = n \log(a) + \log \left[ \frac{1-a}{a} \right] \quad (3)$$

and this is one form of the so-called *Schulz-Flory distribution law*<sup>(7)</sup>. It was first derived by Schulz and Flory in respect of polymerisation and condensation reactions<sup>(19,20)</sup>, and later applied independently to the Fischer-Tropsch reaction by Herington, Friedel, Anderson and others<sup>(21-23)</sup>. If the Schulz-Flory law is obeyed a plot of  $\log(x_n)$  versus  $n$  yields a straight line:  $a$  may be obtained independently from both slope and intercept.  $a$  is usually called the probability of chain growth. However, where the Schulz-Flory law is *not* obeyed values of  $a$  in excess of unity, as determined from Equation (1), may appear, and hence the term is something of a misnomer.

Figures 4 – 7 show industrial and laboratory data plotted in this manner. (NB. The ordinate in these figures is not always  $\log(x_n)$  because some of the data are in terms of mass rather than mole fractions, and some are reported as mass fraction within a certain range of carbon numbers. See Appendix 1). Similar plots are given by Anderson<sup>(5)</sup> for cobalt catalysts and for the Schwarzheide tests conducted in Germany during the war, by Schulz and El Deen<sup>(25)</sup> for the production of alcohols, ketones, etcetera and in numerous other references<sup>(7,26,27)</sup>. It will be seen from these plots that the Fischer-Tropsch reaction does in large measure accord with the Schulz-Flory law; it is often observed, however, that there is a break in the line at some carbon number, and a low  $C_2$  value is quite characteristic. More marked deviations have been reported (see later), but for the moment we stress rather that *agreement with the distribution law has been found for a wide range of catalysts under extremely varied reaction conditions.*

FIGURE 4 Modified Schulz-Flory plot for Sasol fixed-bed reactor  
 [data from Wender<sup>(9)</sup>]



Note:  $1 - W_{cum}$  is the mass fraction of product having a carbon number greater than n.

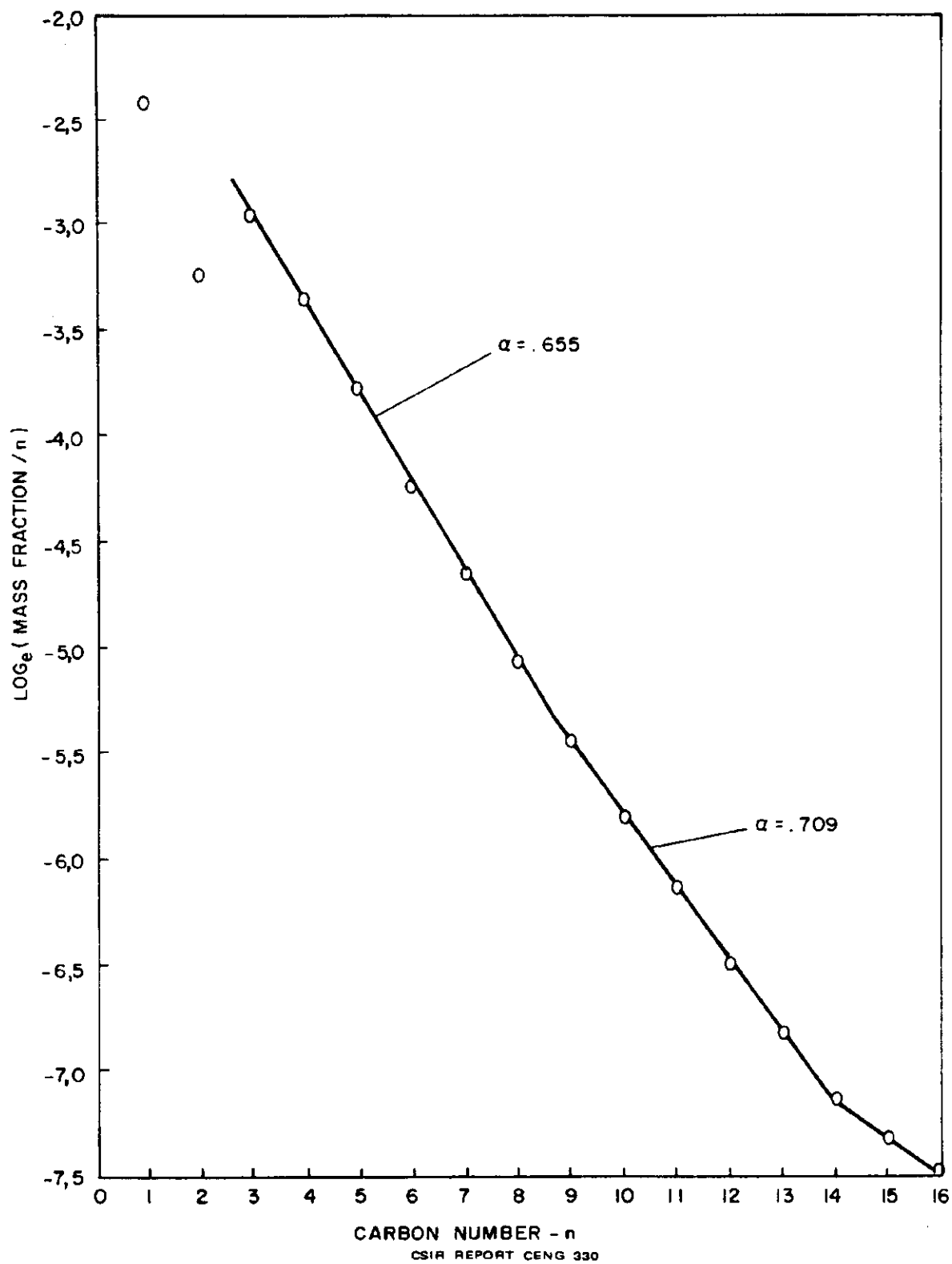
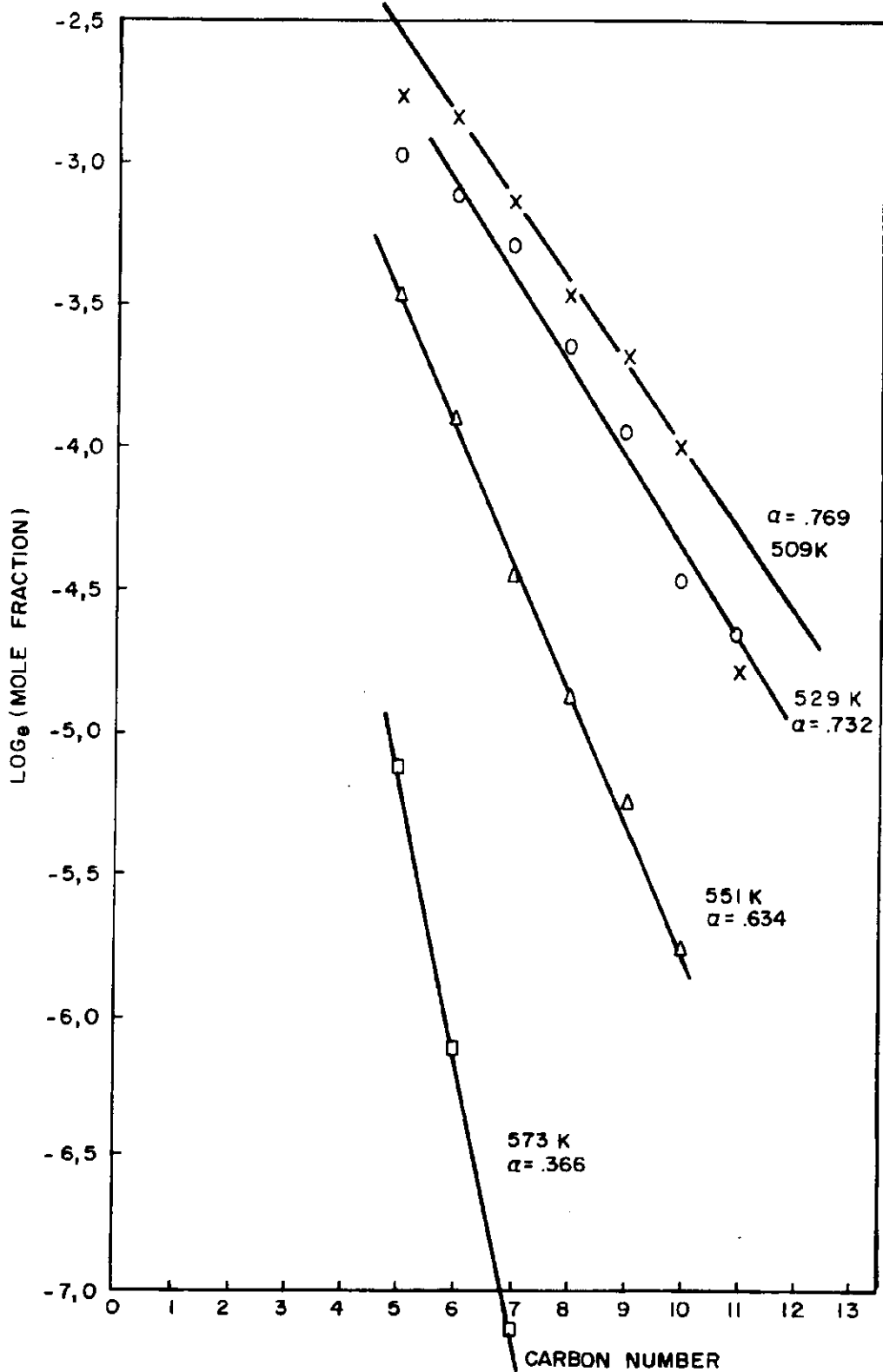
FIGURE 5 Schulz-Flory plot for fluidised-bed pilot plant<sup>(24)</sup>



FIGURE 6 Schulz-Flory plots at various temperatures for a ruthenium catalyst  
in a spinning basket reactor (data taken from Everson et al<sup>(14)</sup>)



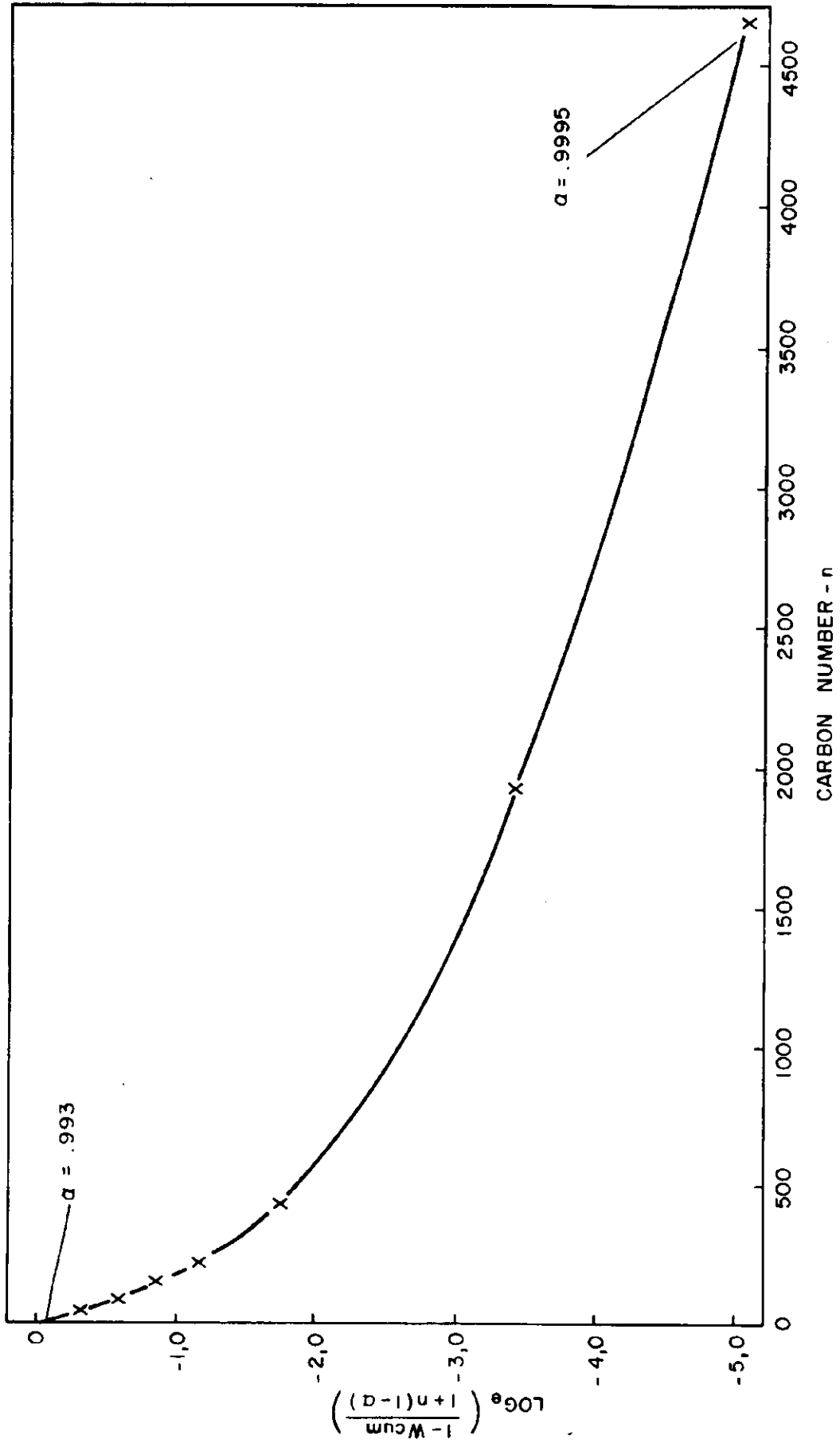


FIGURE 7 Modified Schulz-Flory plot for a ruthenium in n-nonane catalyst at 369 K and 1 000 bar (data from ref. 11) UR

## 2.4 IMPLICATIONS OF THE SCHULZ-FLORY DISTRIBUTION LAW

The non-selective nature of the Fischer-Tropsch reaction is readily understood in terms of the distribution law. So long as this law applies the only optimising variable available to the plant designer is  $a$ . Appendix 1 shows that the mass fraction of product lying within a carbon number range  $a \leq n \leq b$  is given by

$$W_{ab} = (1 - a)(a^{a-1} - ba^b) + a^a - a^b.$$

By differentiating with respect to  $a$  and equating to zero we find the condition that  $W_{ab}$  should be a maximum, namely

$$a^{b-a+1} = \frac{a(a-1)}{b(b+1)}$$

Thus, to maximise the combined gasoline and diesel ( $C_5 - C_{18}$ ) yield we find

$$a^{18-5+1} = \frac{5 \times 4}{18 \times 19} = .05848$$

$$\therefore a = 0,8164$$

**TABLE 4** Theoretical yields according to the Schulz-Flory distribution  
with  $C_5 - C_{18}$  maximised

<b>CARBON NUMBER</b>	1 - 4	5 - 12	13 - 18	19 - 21	22 - 30	> 30
<b>MASS %</b>	22,9	49,0	16,9	4,3	5,4	1,5

Table 4 shows the theoretical yields of the various fractions obtained with this  $a$  value, and it will be seen that the maximum yield of  $C_5 - C_{18}$  cannot exceed 66%.

Compare with these figures the Sasol fixed and transported-bed yields of Table 1 and it appears that they fall on either side of the optimum as here defined — the fixed-bed reactor gives high wax and the transported-bed gives high light ends. The "non-optimality" is exaggerated because for both Sasol reactors the  $a$  value increases at some intermediate carbon number as may be seen, for example, from the break in the line in Figure 4.

When uni-functional catalysts and constant process conditions are employed the Schulz-Flory distribution imposes a constraint on Fischer-Tropsch selectivity. Later in this report ways of overcoming this constraint will be discussed after a brief review of some features of the Fischer-Tropsch process which must be kept in mind.

### 3 CONSIDERATIONS OTHER THAN SELECTIVITY

#### 3.1 ACTIVITY

Reactor size and cost are directly related to the activity of the catalyst. Thus, for example, if we seek to optimise the probability of chain growth by reducing the reactor temperature, there will be a corresponding increase in the reactor size.

This consideration would probably not weigh heavily against improvements in the yield of gasoline and diesel.

#### 3.2 CATALYST LIFE – CARBON DEPOSITION, WAXING, POISONING

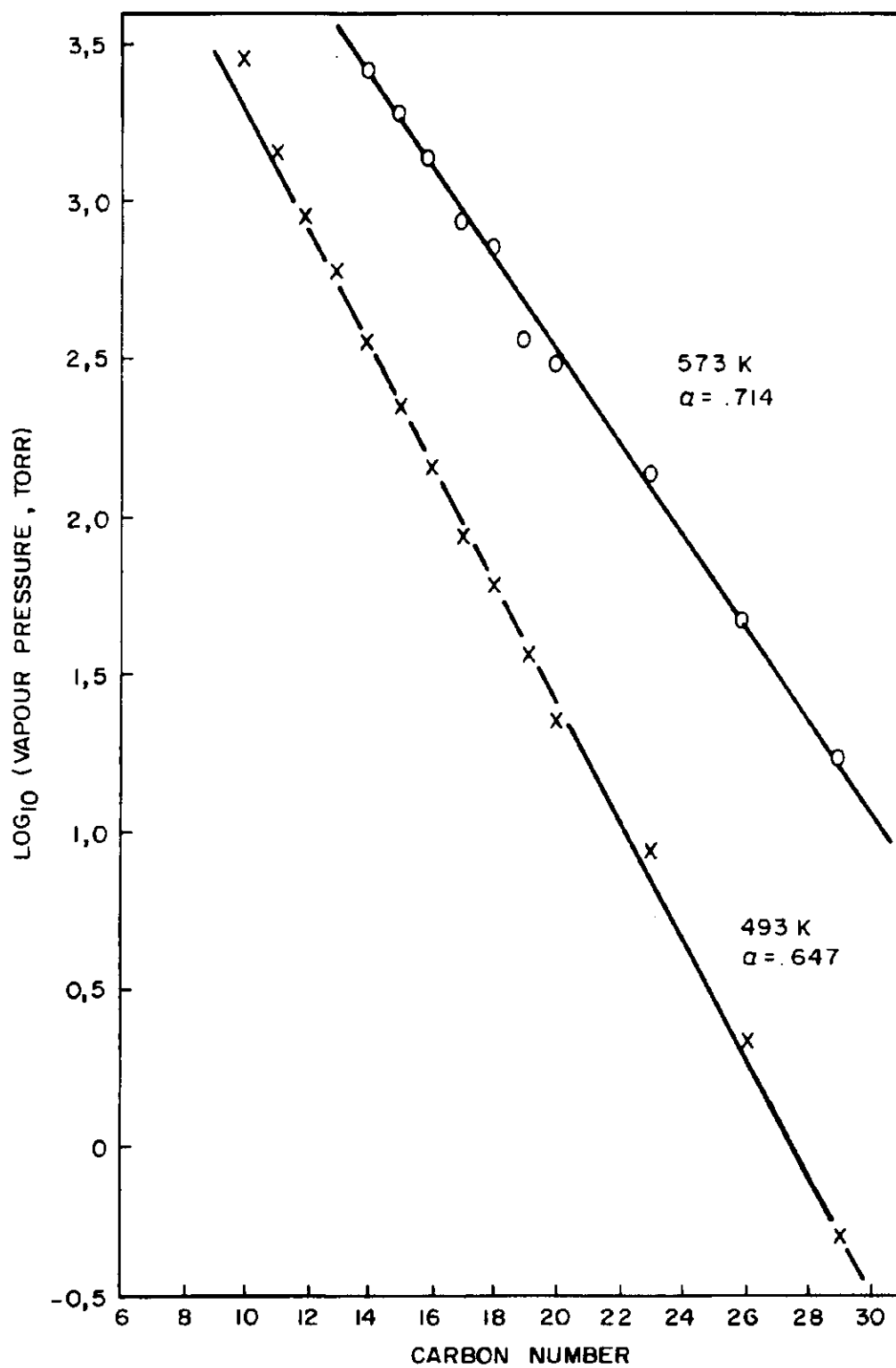
Catalyst life for the Sasol fixed-bed process is said to be six months, during which time the operating temperature is raised<sup>(2)</sup> from 493 to 528 K. Catalysts lose activity due to carbon and/or wax deposition, both of which can also cause plugging of the catalyst bed<sup>(5,6)</sup>. It is not certain whether carbon deposition or waxing is the major cause of loss of activity, but at medium pressures (10 – 20 bar) it appears to be the former<sup>(5)</sup>.

According to Dry carbon deposition occurs more at higher temperatures, whereas one can readily show that waxing is to be expected at low temperatures. A semi-logarithmic plot can be made of the saturation vapour pressure against carbon number for any homologous series such as the normal paraffins (see Figure 8). This gives a straight line of exactly the same form as the Schulz-Flory distribution. Clearly waxing will occur only if the Schulz-Flory plot intersects the vapour pressure plot. Thus, for example, one can deduce from Figure 8 that at a temperature of 493 K only reactors with an  $\alpha$  value in excess of 0,647 will be subject to waxing. (The presence of high molecular mass oxygenated compounds may modify this conclusion).

Avoidance of excessive waxing and carbon deposition may impose lower and upper temperature constraints on the reactor operating temperature.

Fischer-Tropsch catalysts are poisoned by sulphur in the synthesis gas, and sulphur must be reduced to an acceptable level after coal gasification<sup>(1,2,28)</sup>.

**FIGURE 8** Variation of saturation vapour pressure of n-paraffins<sup>(39)</sup>  
with carbon number



The need to replace catalyst periodically — whether due to carbon deposition, waxing or poisoning — is a major process consideration. An expensive catalyst such as ruthenium would need to be recovered after use. Proposed new catalysts must be examined carefully with regard to their initial cost and lifetime under process conditions.

#### 4 IMPROVING FISCHER-TROPSCH SELECTIVITY

The prospects for improving selectivity in the Fischer-Tropsch synthesis seem poor at first sight. The reason for this lies in the facts that

- a. the process of chain growth occurs by one carbon atom at a time, and
- b. because of their chemical similarity intermediate chains of different length on the catalyst surface have almost identical tendencies to grow and to desorb.

Two basic lines of research suggest themselves as a means to overcome the selectivity barrier. The first is to search for a radically new uni-functional catalyst. Such a catalyst (if it exists) would almost by definition have to build the product molecules *other* than by one carbon atom at a time, and it is difficult to visualise a possible process starting from synthesis gas. As a practical proposition we may rule out this line of enquiry.

The second line consists in modifying the basic Fischer-Tropsch distribution pattern either by use of a bi-functional catalyst or by a cyclical processing operation. In both cases the objective may be formally expressed as

$$\begin{array}{ll} a \rightarrow 1 & 0 < n \leq a \\ a \rightarrow 0 & n > a \end{array}$$

where  $a$  is some pre-selected carbon number of the order of 18 if the yield of gasoline and diesel is to be maximised.

##### 4.1 BI-FUNCTIONAL CATALYSTS

Under uniform steady state conditions with a uni-functional catalyst only one value for  $a$  can be attained. It may be possible to introduce other functions into the catalyst so that, for instance, growth beyond a certain carbon number is cut off in one way or another.

Investigations by Uytterhoeven et al<sup>(29)</sup>, not reported in great detail, suggest that by incorporating the Fischer-Tropsch catalyst within the cages of a zeolite structure a size restriction can be placed on chain growth.

**TABLE 5** Product distribution over a Ru-NaY zeolite at 525 K  
and 14,2 bar (approximate)<sup>(29)</sup>

CARBON NUMBER	1-4	5	6	7	8	9	10	11	>11
MASS %	30,0	9,5	7,7	10,7	6,1	6,8	7,6	7,5	14,1

Table 5 shows the (approximate) mass fractions obtained by them when reacting a 3:2 H<sub>2</sub>/CO mixture over a Ru-NaY zeolite at 525 K and 14,2 bar. Less than 1 mole % of the products were in the range C<sub>11</sub>+. They state that the chain limitation was not due to hydro-cracking. A similar result was obtained with a Ru-LaY zeolite, except that chain limitation occurred after C<sub>5</sub> and this was attributed to the smaller ruthenium metal particle size. A feed of n-dec-1-ene was passed over the same catalyst at the same temperature (but at lower pressure and considerably higher space velocity): no cracking occurred but the dec-1-ene was isomerized in various ways.

A non-Schulz-Flory distribution has been reported also by Madon working with a 2:1 H<sub>2</sub>/CO mixture reacting on a 1% Ru on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 3,1 bar and 514 K<sup>(30)</sup>. Figure 9 shows the distribution found by him together with the Schulz-Flory distribution having a maximum at C<sub>10</sub> - C<sub>11</sub>. The difference is striking. One wonders if a cracking reaction on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> may account for this, but if so there is obviously no cracking to methane.

Two recent papers<sup>(31,32)</sup> are related to a number of patents assigned to Mobil<sup>(33,36)</sup>. Catalysts were prepared from mixtures of a ZSM-5 zeolite with a Fischer-Tropsch metal in the following ways:

1. By vacuum impregnation of the zeolite with metal nitrate solution, followed by drying and calcining.
2. By milling together the metal component and the zeolite prior to pelleting and calcining.
3. By physically mixing particles of zeolite with a commercial potassium promoted ammonia synthesis catalyst.

The catalysts were tested in fixed-bed microreactors (4 - 10 ml of catalyst).

**FIGURE 9** Product distribution on a 1% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst  
at 3,1 bar and 514 K(30)

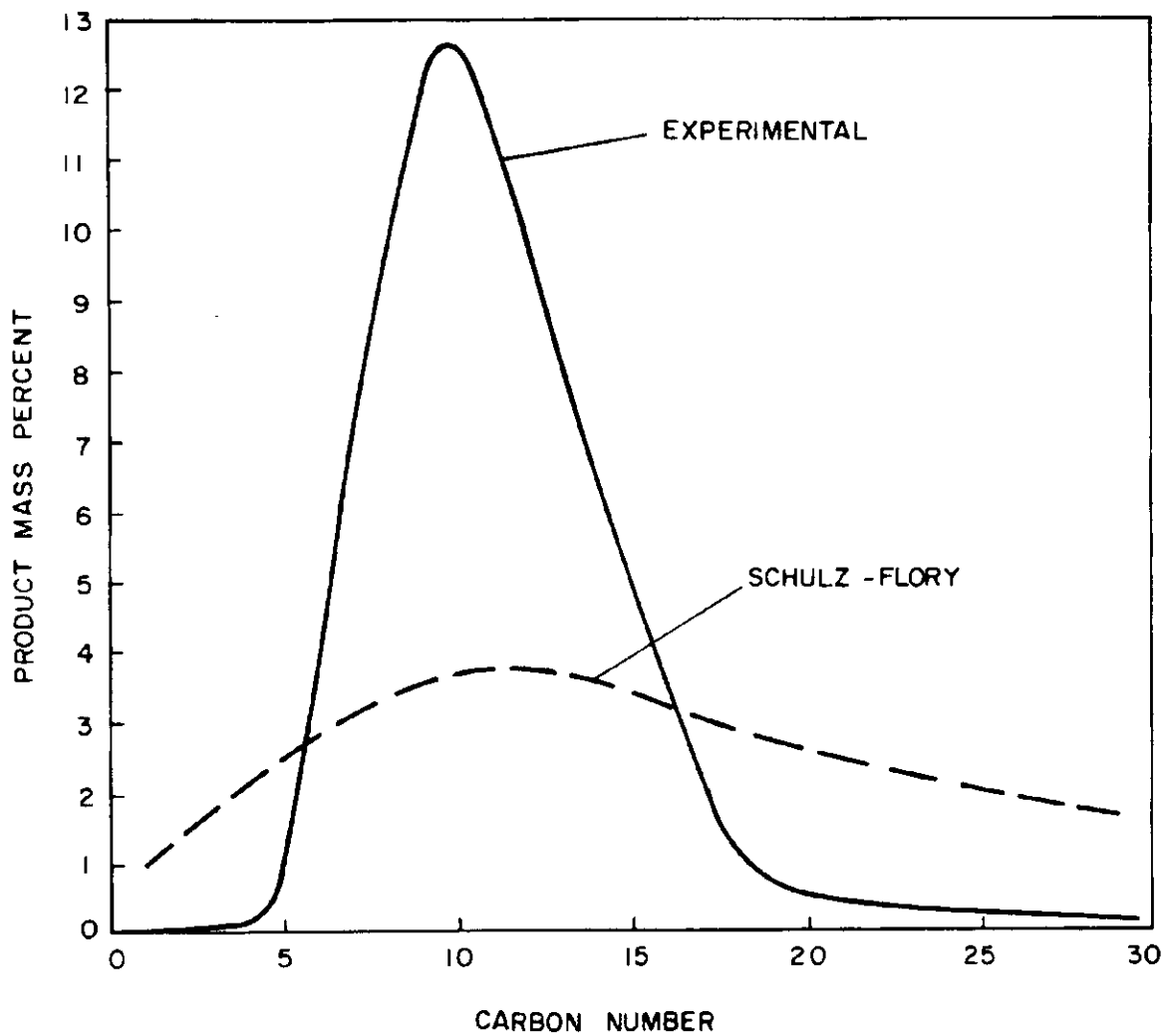




TABLE 6 Product distribution with Zn-Cr/Zeolite mixed catalysts(H<sub>2</sub>:CO = 1:1)<sup>(31)</sup>

<b>Catalyst</b>			
Metal component	Zn-Cr	Zn-Cr	Zn-Cr
Zeolite	None	ZSM-5	ZSM-5
Component particle size-mesh	- 60	60/80	- 200
<b>Reaction conditions</b>			
Temperature - K	700	700	700
Pressure - bar	84	84	84
Space velocity - hr <sup>-1</sup>	1 740	1 780	1 780
<b>Conversion (H<sub>2</sub> + CO) - mole %</b>	18,9	44,1	37,7
<b>Product distribution - mass %</b>			
C <sub>1</sub>	42,2	3,9	2,5
C <sub>2</sub>	9,8	13,1	12,3
C <sub>3</sub>	3,8	22,9	9,9
C <sub>4</sub>	1,8	15,5	3,3
C <sub>5</sub> <sup>+</sup>	4,9	44,6	72,0
Oxygenates	37,5	< 0,1	-
Percent olefins in product	2,8	0,6	0,1
Percent aromatics in C <sub>5</sub> <sup>+</sup>	0	75,6	97,3

Table 6 shows the results of a test on a catalyst consisting of a physical mixture of 60/80 mesh particles of Zn-Cr and zeolite. Compared with Zn-Cr alone the conversion is doubled, methane formation is greatly reduced, oxygenates are eliminated and large quantities of C<sub>5</sub><sup>+</sup> aromatics are formed. In the same table is shown the effect of milling the Zn-Cr and zeolite components to -200 mesh and pelleting the mixture: the shift in product distribution indicates some diffusional effects.

**TABLE 7** Effect on product distribution of varying the ratio and spatial arrangement of the components of an iron/zeolite mixed catalyst<sup>(32)</sup>

Experiment Fe/Zeolite/Quartz (by vol.)	1 1/4/0		2 1/4/20		3 1/0/4		4 2,5/2,5/0		5 1/0/4/0/0/4/0/4/0	
	2	5	2	5	1	2	2	4	1	3
Time on stream (days)					76	18	97	Plug	25	14
CO Conversion (mass %)	95	94	98	90	76	18	97	Plug	25	14
H <sub>2</sub> Conversion (mass %)	54	49	56	40	47	Plug	58	—	16	Plug
Product (mass %)										
Total hydrocarbons	53	61	56	58	40	40	52	—	61	—
Aromatics	40	20	30	24	Trace	Trace	30	—	30	—
Olefins	3	36	14	38	84	82	Trace	—	Nil	Nil
Oxygen	0.1	—	—	—	—	1,4	—	—	—	—

In Table 7 the effect of changing the spatial configuration of the components of an iron/zeolite mix is shown. In the first experiment the iron and zeolite particles were intimately mixed in 1:4 ratio. The second experiment used the same mix heavily diluted with quartz particles; results are almost identical which indicates, according to the authors, that stable intermediate molecules are involved. Neither of these tests resulted in any waxing of the catalyst. In the third experiment particles of quartz were substituted for the zeolite and the catalyst bed plugged with wax in two days. Experiment four used an excess of iron particles relative to zeolite and again wax formation occurred. In experiment five the iron catalyst was separated from the zeolite by an intermediate layer of quartz, giving low conversion and wax plugging.

The authors of these papers suggest that the function of the zeolite is to intercept molecular intermediates and convert them to forms resistant to further chain growth; they propose that the intermediates are  $\alpha$ -olefins which are converted principally to aromatics. This theory accords with the view of Dwyer and Somorjai<sup>(26)</sup> that "re-adsorption and secondary reaction of  $\alpha$ -olefins is an important pathway leading to the formation of large molecular weight hydrocarbons".

Clearly the use of bi-functional catalysts offers interesting possibilities for Fischer-Tropsch development.

#### 4.2 CYCLICAL PROCESSING

Fischer-Tropsch synthesis is not by any means a rapid reaction and we may profitably ask how long it takes to build up the steady state product spectrum starting from a clean but activated catalyst surface. The following simple model of the growth process provides some information.

Imagine the surface to consist of a fixed number of cells,  $N$ , each cell corresponding to an active site. At the beginning of the process we commence to add balls to the cells in random fashion but at a fixed rate,  $y$  per second. Each ball placed in a cell corresponds to the addition of one carbon atom to a growing chain. Simultaneously we start to empty the contents of the cells, also in random fashion, at a fixed rate,  $x$  per second; this models the desorption process.

Let  $q$  = Mean number of balls per cell at time  $t$  ( $q$  is thus the average chain length on the surface at any moment of time).

$$ydt - xqdt = Ndq \quad (4)$$

Re-arranging and integrating

$$\frac{N}{x} \log_e \left[ \frac{y}{y - xq} \right] = t \quad (5)$$

When the process reaches steady state conditions the average chain length is constant,  $dq = 0$ , and hence from Equation (4)

$$q = \frac{y}{x}$$

Equation (5) shows that the time required to reach this condition is infinite. Let us therefore define a half-time,  $t_{1/2}$ , as the time required for the average chain length to reach half its ultimate value.

$$\therefore t_{1/2} = \frac{N}{x} \log_e \left[ \frac{y}{y - 0.5y} \right] = \frac{N}{x} \log_e 2 = 0.6931 \frac{N}{x}$$

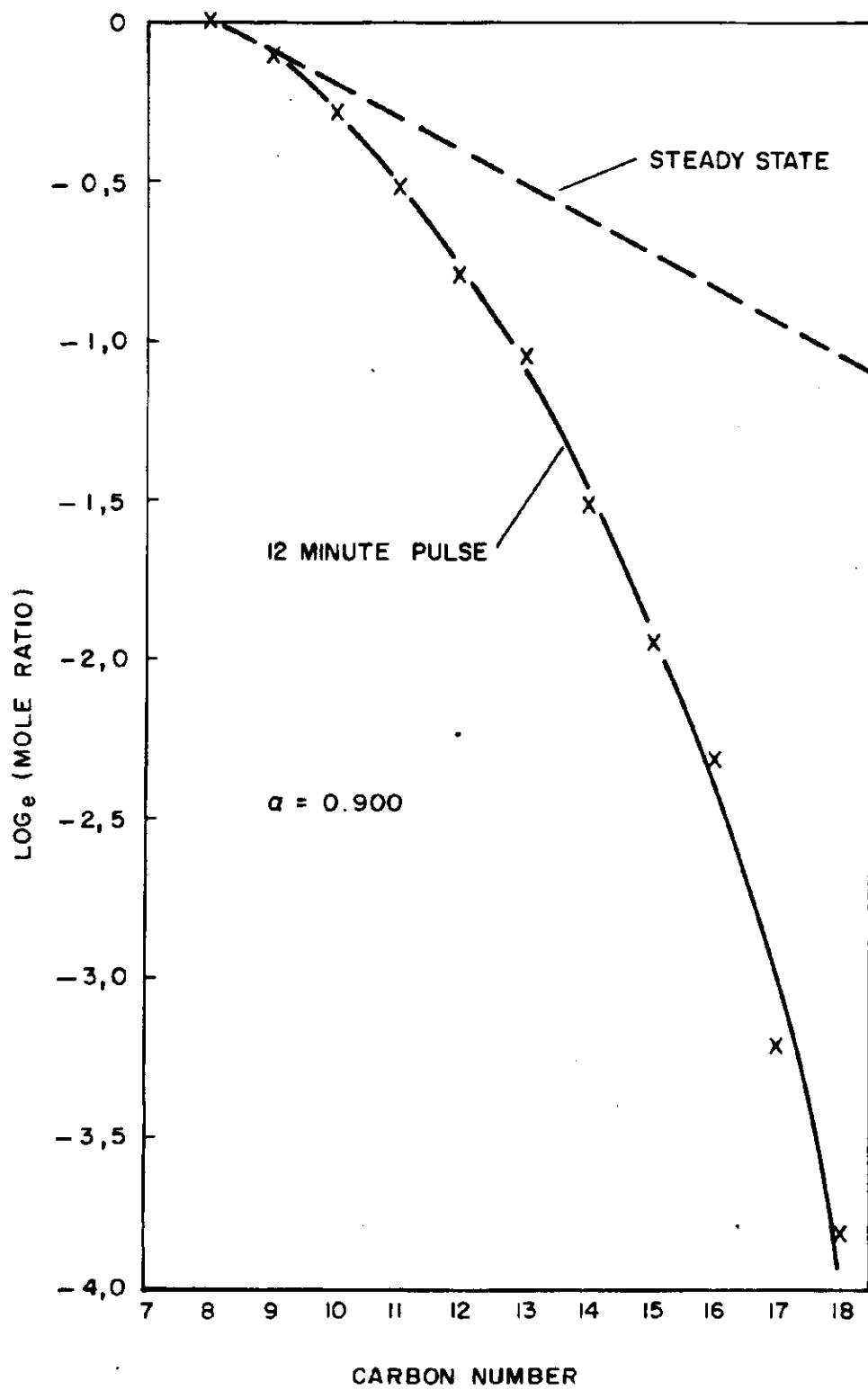
$$\begin{aligned} \text{Now } \frac{x}{N} &= \text{Molecules desorbed per site per second} \\ &= \text{Turnover number for total hydrocarbons (N}_{\text{HC}}) \end{aligned}$$

$$\therefore t_{1/2} = \frac{0.6931}{N_{\text{HC}}} \quad (6)$$

Vannice<sup>(4)</sup> has reported turnover numbers for *methane* formation on various catalysts, but under conditions where methane was the major product, and these are of the order  $20 \times 10^{-3}$  per second at 548 K. Using this value gives a half-time for the process of 35 seconds, which increases to 197 seconds at 493 K. (Activation energy  $\sim 71$  KJ/mole). Bearing in mind that these are *half-times* it seems that several minutes may be required before the distribution on the catalyst surface approaches closely to the steady state.

This being so it may be possible to limit chain growth by operating a reactor under cyclic process conditions such that  $\alpha \rightarrow 1$  during the growth part of the cycle. At the end of the cycle conditions in the reactor must be rapidly altered in such a way that the products desorb as completely as possible, and a further growth cycle is initiated. It would be quite impractical to cycle a large catalyst mass through an appreciable temperature difference : therefore the process variables would probably be limited to total pressure and  $\text{H}_2/\text{CO}$  ratio. Sastri and Srinivasan found that wax adsorbed on a cobalt catalyst could be removed by evacuation at 473 K<sup>(37)</sup> : it may be possible to remove lower molecular weight hydrocarbons (up to, say,  $\text{C}_{25}$ ) by dropping the total pressure to one atmosphere.

Dautzenberg et al have used a pulse technique to determine Fischer-Tropsch kinetics<sup>(38)</sup>. They used eight and twelve minute pulses of synthesis gas (1:1  $\text{H}_2/\text{CO}$ ) at 483 K and ten bar over a ruthenium on  $\gamma\text{-Al}_2\text{O}_3$  catalyst. Each pulse of synthesis gas was followed by reduction in hydrogen with a gradual rise in temperature to 623 K. Hydrocarbon products from many such pulses were collected and analysed and gave distribution plots as indicated in Figure 10. It is seen that the products are relatively low in high molecular weight hydrocarbons as compared with the steady state distribution. (In one experiment with eight minute pulses a  $\text{C}_{12}/\text{C}_6$  ratio of 0.12 was found, compared with the steady state value of 0.74).

FIGURE 10 Chain termination by pulsing<sup>(38)</sup>

In Appendix 2 equations are developed to describe the change in surface population of the catalyst with time, using the basic model of Fischer-Tropsch previously presented. Figure 11 shows the change in site population of  $C_1$  and  $C_2$  intermediates with (dimensionless) time for a particular value of chain growth probability. Note that the  $C_2$  population actually *exceeds* the  $C_1$  population over a certain period. The equations developed can be integrated to give the total quantity of each product formed in any time interval, and can also be used to determine the quantities present on the surface at the end of that interval. Figure 12 shows a distribution plot indicating for a particular choice of parameters

- a. distribution of products desorbed over a period,
- b. distribution on the surface at the end of that period,
- c. combined weighted product distribution, i.e. the sum of (a) and (b) weighted according to the relative quantities.

(In this case the relative quantities are almost equal). Table 8 shows the corresponding mass fractions for various product "cuts" compared with the steady state values at the same chain growth probability.

TABLE 8

Product range	$C_1 - C_4$	$C_5 - C_{12}$	$C_{13} - C_{18}$	$C_{19} - C_{21}$	$> C_{21}$
Steady state mass %	2,06	10,44	10,33	5,38	71,79
Transient mass %	7,75	41,79	39,17	7,90	3,39

The results of Dautzenberg are in part a confirmation of the theory presented in Appendix 2; however, he seems not to have recovered any appreciable amounts of the product on the surface at the end of a pulse. If these amounts are comparable to what is desorbed during the pulse this constitutes a serious loss. Further experimental work is needed to evaluate the situation.

FIGURE 11 Variation of catalyst surface population with time

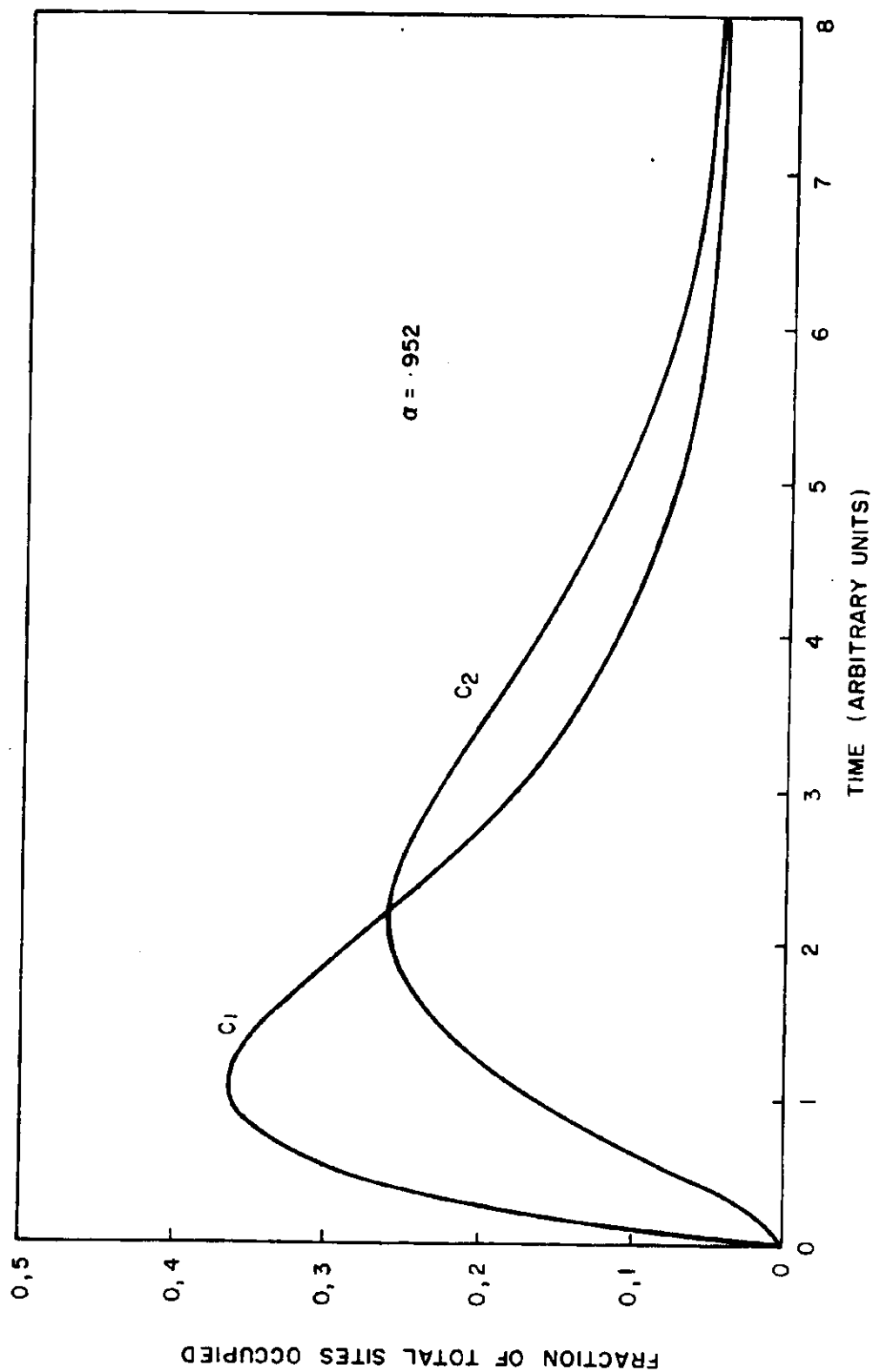
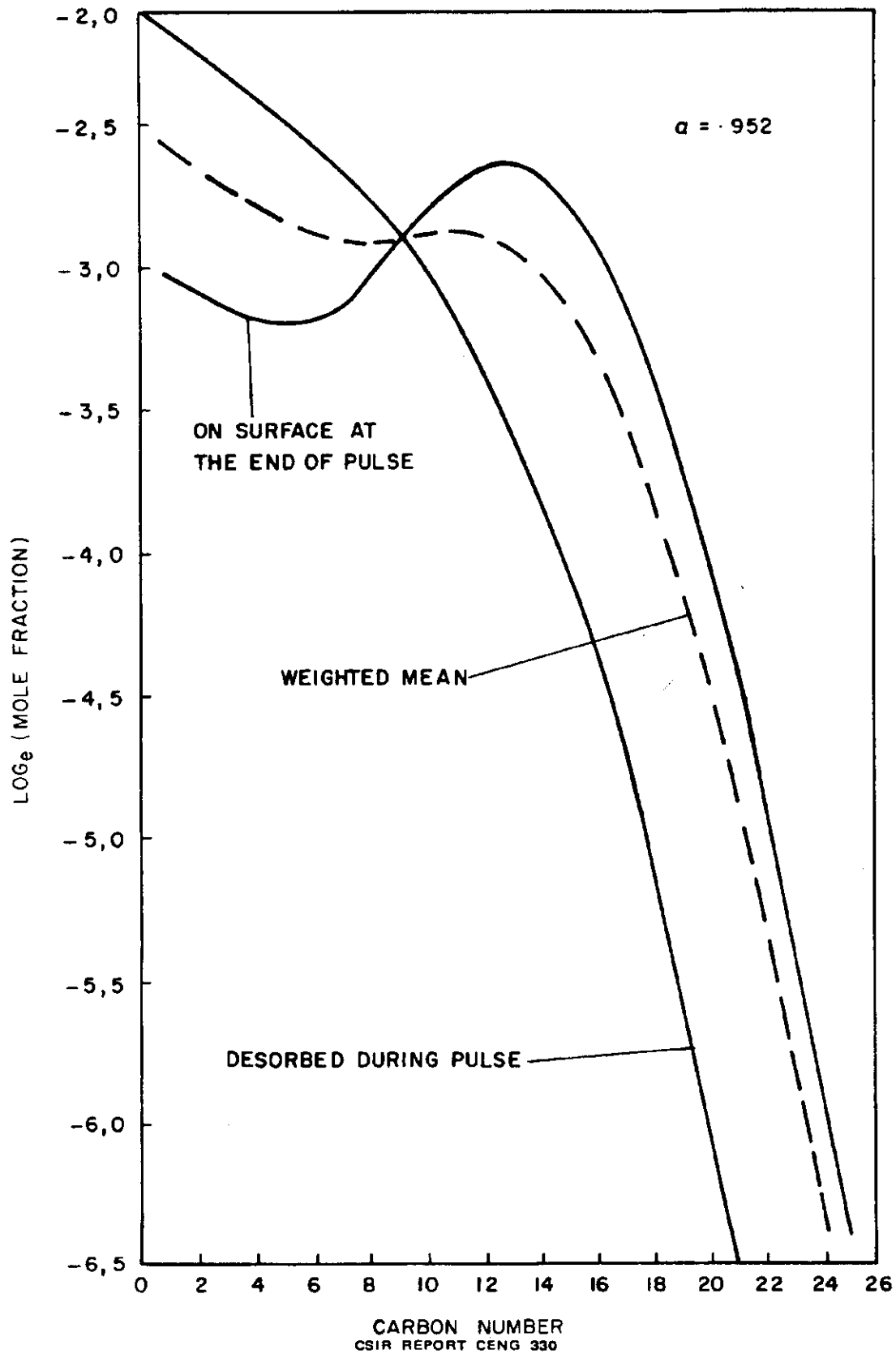


FIGURE 12 Product distribution from a pulsed catalyst





**5** CONCLUSIONS

1. The Fischer-Tropsch reaction on uni-functional catalysts is non-selective; a narrow product distribution cannot be obtained.
2. Catalyst poisoning and de-activation make replacement cost of the catalyst a major consideration. Iron catalysts are favoured for this reason.
3. A simple model of the Fischer-Tropsch reaction involving chain growth by one carbon atom at a time enables one to predict the pattern of the product distribution (Schulz-Flory distribution law) under steady state conditions. This pattern is shown by a wide range of catalysts over a wide range of conditions.
4. The distribution pattern imposes an upper limit on the steady state selectivity for any product range.
5. Adherence to the distribution pattern may be circumvented by use of dual-function catalysts or by operating under non-steady state conditions.

**6** RECOMMENDATIONS

1. That the Fischer-Tropsch reaction be studied experimentally under reaction conditions which simulate industrial practice as closely as possible with a view to improving selectivity for diesel and gasoline by the use of dual-function catalysts.
2. That an appraisal be made of the effect of operating the Fischer-Tropsch reaction under transient process conditions.

7 APPENDIX7.1 RELATIONS DERIVED FROM THE SCHULZ-FLORY LAW

As shown already the mole fraction of carbon number  $n$  is given by

$$x_n = a^{n-1}(1-a)$$

Approximating the reaction by a condensation of  $-\text{CH}_2-$  units (MW = 14) the corresponding mass is given by

$$W_n = 14na^{n-1}(1-a)$$

and the mass fraction by

$$W_n = \frac{W_n}{\sum_1^{\infty} W_n}$$

$$\begin{aligned} \sum_1^{\infty} W_n &= 14(1-a) \sum_1^{\infty} na^{n-1} \\ &= 14(1-a) \left[ \frac{1}{1-a} \right]^2 \\ &= \frac{14}{1-a} \end{aligned}$$

$$\therefore W_n = na^{n-1}(1-a)^2$$

$$\text{and } \log \left[ \frac{W_n}{n} \right] = n \log(a) + \log \left[ \frac{(1-a)^2}{a} \right]$$


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The mass fraction,  $W_{ab}$ , lying in the range  $a \leq n \leq b$  is given by

$$\begin{aligned} W_{ab} &= \sum_a^b na^{n-1}(1-a)^2 \\ &= (1-a)^2 \sum_a^b na^{n-1} \\ &= (1-a)^2 \left[ aa^{a-1} + (a+1)a^a + \dots + (b-1)a^{b-2} + ba^{b-1} \right] \\ aW_{ab} &= (1-a)^2 \left[ aa^a + (a+1)a^{a+1} + \dots + (b-1)a^{b-1} + ba^b \right] \\ \therefore (1-a)W_{ab} &= (1-a)^2 \left[ aa^{a-1} + a^a + a^{a+1} + \dots + a^{b-1} - ba^b \right] \end{aligned}$$

$$\text{Let } S = a^0 + a^{0+1} + \dots + a^{b-1}$$

$$aS = a^{0+1} + a^{0+2} + \dots + a^b$$

$$\therefore (1-a)S = a^0 - a^b$$

$$\therefore W_{a,b} = \frac{(1-a)(a^{b-1} - ba^b) + a^0 - a^b}{1 + b(1-a)}$$

In particular, if  $a = 1$

$$\begin{aligned} W_{1,b} &= (1-a)(1 - ba^b) + a - a^b \\ &= 1 - a^b(b - ba + 1) \end{aligned}$$

$$\text{or } 1 - W_{1,b} = a^b[1 + b(1-a)]$$

$$\log \left[ \frac{1 - W_{1,b}}{1 + b(1-a)} \right] = b \log(a)$$

This equation cannot be directly graphed because the left hand side contains the unknown  $a$ . However, if a first approximation to  $a$  can be obtained (e.g. by considering the initial part of the line where  $b$  is small and the correction  $1 + b(1-a)$  is negligible) then a method of successive graphical approximation can be employed which converges to give a "best plot" of the data. This technique has been used in preparing Figures 4 and 7.

## 7.2 CHANGE IN CATALYST SURFACE POPULATION WITH TIME

- Let
- $N$  = Total number of available sites
  - $N_o$  = Number of vacant sites
  - $N_n$  = Number of sites occupied by chains of length  $n$
  - $y$  = Carbon units added per second
  - $x$  = Molecules desorbed per second

$$\therefore \frac{dN_o}{dt} + \frac{N_o(x+y)}{N} = x$$

(Since  $dN_o$ , the net number of vacant sites created in time  $dt$ , is equal to the number of vacant sites created by desorption less the number filled by addition of a carbon unit).

The solution of this linear first order differential equation is

$$\frac{N_o}{N} = \frac{x}{x+y} - \left[ \frac{x}{x+y} - 1 \right] \exp \left[ - \frac{x+y}{N} t \right]$$

which can be simplified to

$$\frac{N_o}{N} = \frac{1}{1+q} \left[ 1 + q \exp(-Kt) \right]$$

where  $q = \frac{y}{x}$  and  $K = \frac{x+y}{N}$

Similarly

$$\frac{dN_1}{dt} + \frac{N_1(x+y)}{N} = \frac{y}{N} N_o$$

$$\frac{dN_1}{dt} + KN_1 = \frac{y}{N} N_o = \frac{y}{N} \frac{1}{1+q} [1 + q \exp(-Kt)]$$

which has the solution

$$\frac{N_1}{N} = \frac{q}{(1+q)^2} [1 + (qKt - 1) \exp(-Kt)]$$

Similarly

$$\frac{N_2}{N} = \frac{q^2}{(1+q)^3} \left[ 1 + \left[ \frac{q(Kt)^2}{2!} - Kt - 1 \right] \exp(-Kt) \right]$$

$$\frac{N_3}{N} = \frac{q^3}{(1+q)^4} \left[ 1 + \left[ \frac{q(Kt)^3}{3!} - \frac{(Kt)^2}{2!} - Kt - 1 \right] \exp(-Kt) \right]$$

and by induction

$$\frac{N_n}{N} = \frac{q^n}{(1+q)^{n+1}} \left[ 1 + \left[ \frac{q(Kt)^n}{n!} - \frac{(Kt)^{n-1}}{(n-1)!} - \dots - Kt - 1 \right] \exp(-Kt) \right]$$

(1)

To determine the total production (desorption) of molecules of length  $n$  over the interval  $0 \rightarrow t$  we require to evaluate

$$\phi_n = \int_0^t \frac{x}{N} N_n dt$$

where  $N_n$  is a function of  $t$  as given above. The integration is tedious but the solution is

$$\phi_n = \frac{xq^n}{K(1+q)^{n+1}} \left[ Kt + (q-n) - \exp(-Kt) \left[ \frac{q(Kt)^n}{n!} + \frac{q-1}{(n-1)!} (Kt)^{n-1} + \dots + \dots + (q-n+1)Kt + (q-n) \right] \right] \quad (2)$$

Equations (1) and (2) have been used to determine the mole fractions of components up to  $C_{22}$  which are retained on the surface at the end of a pulse and desorbed during the pulse respectively. The duration of the time interval was from  $Kt = 0$  to  $Kt = 15$ , and a value of  $q = 20$  was chosen. (One can readily show that

$$q = \frac{a}{1-a}$$

and hence this value of  $q$  corresponds to a chain growth probability of 0,9524). The relative amounts desorbed and retained can be determined from the relation

$$\frac{\text{Moles of } n \text{ retained on surface}}{\text{Moles of } n \text{ desorbed}} = \left[ \frac{q+1}{Kt} \right] \left[ \frac{\text{Mole fraction } n \text{ on surface}}{\text{Mole fraction } n \text{ desorbed}} \right]$$

The results are shown in Figure 12.

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