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SELECTIVE NAPHTHENE PYROLYSIS FOR ETHYLENE WITH HYDROGEN AS DILUENT

A.A SUSU and A F. OGUNYE

Chemical Engineering Department, University of Lagos, Lagos (Nigeria)

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ABSTRACT

Thermal decomposition of a heavy Nigerian naphthenic naphtha and cyclohexane was investigated in a flow system with stainless steel tubular reactors in the presence of hydrogen. The pyrolysis conditions were· atmospheric pressure, temperatures ranging between 630 and 900°C, constant space time of 0.03 sec, hydrogen. liquid ratio of 7 and 28 for naphtha and 20 for cyclohexane, and surface to volume ratios of 8 and 21.5 cm^{-1} The main products of the pyrolysis reaction were ethylene, propylene, butadiene and methane. The ethylene yield was enhanced in the presence of hydrogen. At temperatures between 820 and 850°C, the ethylene yield was increased from 0 238 to 0.528 for a four-fold increase in hydrogen to naphtha ratio. The coke yield was found to go through a maximum at temperatures between 780 and 800°C, depending on the hydrogen naphtha ratio As the effect of surface was minimized by increasing tube size or the addition of CS_2 to a given tube size, both ethylene and coke yield were reduced while methane yield was increased.

INTRODUCTION

Paraffinic naphtha is the preferred liquid feedstock for the petrochemical industry because of the high ethylene yield resulting from its pyrolysis. Thus, the pyrolysis of paraffinic naphtha and pure paraffins has been subjected to considerable laboratory study and the mechanism of olefin production from pure paraffins is reasonably well understood [1]. Work on the pyrolysis of naphthenic feedstocks has not received the same level of attention and the kinetics of the decomposition of pure naphthenes at high temperatures to olefins has not been well established.

Pyrolysis of naphthenic feedstocks is known to result in substantial butadiene yield and the earlier publications were directed towards experimental investigation of the optimum operating conditions for butadiene production [2—4]. Product distribution for the pyrolysis of heavy naphthenic naphtha was published recently with very little information about the effect of process conditions on olefin yields [5]. Primary product distribution has only been determined for some pure napthenes [6,7]. The scarcity of data on the pyrolysis of pure naphthenes and mixtures of liquid naphthenes needs to be remedied because the yield of decomposition products of liquid paraffin feedstocks may be influenced by its naphthenic content. For example, typical paraffinic naphthas usually contain as much as 20 wt.% cycloparaffins.

Furthermore, the present unpreditacle petroleum market dictates that new pyrolysis furnaces must be designed for feedstock flexibility from gas to liquid feeds [8]. This flexibility must of necessity include various types of naphthas to adequately provide detailed product spectra for semi-empirical modelling of commercial furnace design from laboratory pyrolysis data [9, 10]. Published works in laboratory investigation of naphthenic naphthas and pure naphthenes has not kept up with this reality.

Recent studies on the effect of surface on product yields from laboratory pyrolysis furnaces have highlighted the problem inherent in extrapolating laboratory pyrolysis data for commercial use. The formation of coke catalyzed by the material of construction of the pyrolysis furnace has been investigated extensively for some light paraffins and propylene [11]. The problem of coke formation in the pyrolysis furnace is even more acute for naphthenic feedstocks. No study to date, as far as the authors are aware, has investigated the behaviour of coke formation with process conditions and material of furnace construction for naphthenic feeds.

In this paper, we report our investigation on the pyrolysis of a naphthenic feedstock (Nigerian heavy naphtha) using hydrogen as a diluent. We also studied the pyrolysis of cyclohexane under similar process conditions. We focussed on specification of the product yields as functions of furnace temperature with particular emphasis on metal-catalyzed carbon formation

EXPERIMENTAL

Materials

The heavy naphthenic naphtha used in this investigation was the Umuechem/TNP naphtha cut from the atmospheric distillation tower of the Nigerian Petroleum Refining Company. The specifications and compositions of the feed naphtha are shown in Table 1. The PNA analysis is 30.7% paraf-

TABLE 1

Specification and composition of a Nigerian heavy naphtha

Specific gravity		0 7594
ASTM distillation (°C)	IBP	114.0
	10%	121.0
	50%	131.0
	90%	151 5
	EP	172 0
Residue (vol.%)		1.0
Hydrocarbon type analysis (vol.%)		
	Paraffin	31.0
	Naphthene	50 0
	Aromatics	19.0

fins, 50.4% cycloparaffins and 18.9% aromatics. Research grade cycloparaffin from Fisons Scientific Apparatus was used as a liquid feed and high purity cylinder hydrogen from Industrial Gases, Lagos was used without further purification.

Analysis

Product samples were analyzed chromatographically using a Perkin-Elmer Model 900 GC with dual flame ionization and thermal conductivity detectors. A Perkin-Elmer SIP-1 storing integrator was used for peak-evaluation. Two columns were used for the analysis of gaseous effluent from the laboratory pyrolysis furnace. The C_1—C_3 hydrocarbons (methane, ethane, ethylene, propane, acetylene, propylene and 1,2-propadiene) were analyzed by use of a 1 m X 2.3 mm I.D. phenylisocyanate/porasil C 80/100 mesh column. A 1.5 m X 2.3 mm I.D. N-octane/porasil C 120/150 mesh column was used to analyze gaseous components of the C_1—C_4 isomers (methane, ethane and ethylene, acetylene, propane, propylene, isobutane, butane, butene-1, butadiene butene-2). Both columns were operated at 23°C and placed on three-way valve to facilitate analysis by switching from one column to the other.

Apparatus and procedure

The flow system used in this investigation is shown in Fig. 1. Hydrogen and naphtha (or cyclohexane) were mixed and preheated before entering the reactor at atmospheric pressure. Because low liquid hydrocarbon flow rates were used in this investigation, an HPLC pumping system from Chemical Data Systems was used for controlling liquid hydrocarbon feed rate. This pump is capable of delivering liquid feedstocks at steady rates between 16 and 160 ml/h. against a back pressure as high as 3000 psi. Both the reactor

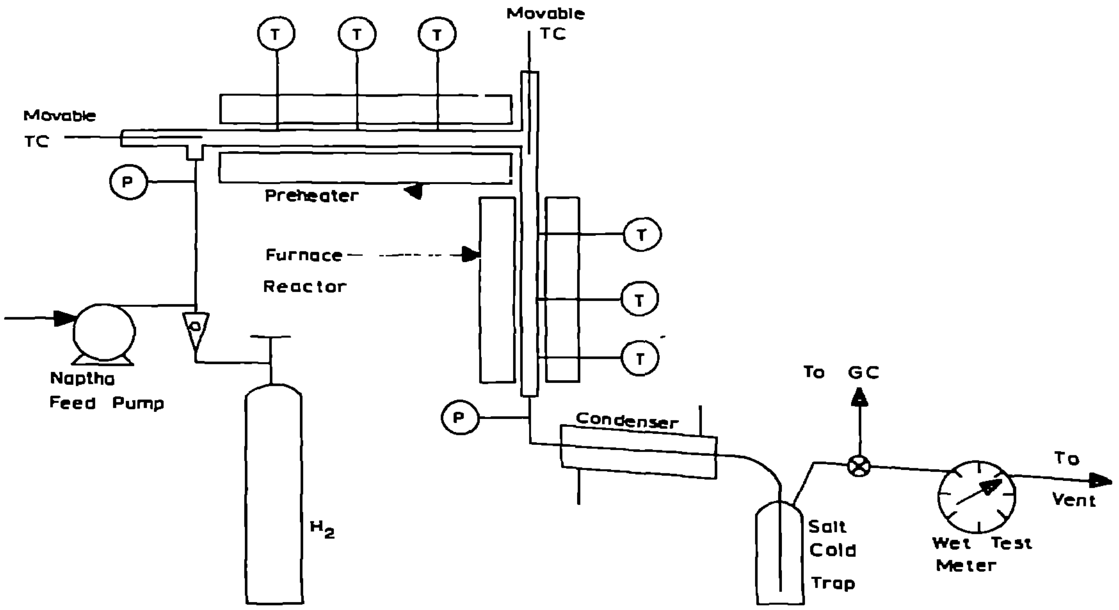

Fig. 1. Schematic diagram of the pyrolysis apparatus.

and the preheater were 304 stainless steel tubings; two reactor types were used. The first reactor was of the annular type with the o.d. of the inner 1/8-in tubing being 3.14 mm. and the i.d. outer 1/4-in tubing being 5.0 mm. The second reactor was an open 1/4-in tubing. The surface to volume (S/V) ratios of the annular and open tubular reactors were 21.5 and 8.0 cm^{-1}, respectively. Both the reactor and preheater temperatures were controlled by regulating the heat input of two Stanton Redcroft electric furnaces with feedback temperature controllers. The temperature profile along the outside wall of the reactor was monitored at four locations by use of Pt—Pt Rh thermocouples. For the annular reactor the axial temperature profile was also monitored during each run. The temperature profile was generally flat for the middle third of the 30 cm reactor length and this temperature was used throughout as the pyrolysis furnace temperature.

The gaseous effluent was passed through a condenser and the liquid products were trapped in a salt cold trap. The non-condensable gases were lead through a sampling valve into the gas chromatograph for analysis.

Each experimental run was conducted under steady state and a run was terminated before coke formation in the reactor caused significant deviation from steady state. The onset of unsteady state behaviour was determined from noticeable variation in the chromatograms of the components of the gaseous effluents and/or the flow rate of the effluent gas stream. Typically, the first gas sampling was done 5 min after the start of a run. Subsequent gaseous sampling was then done at 10-min intervals. Generally, steady state was attained within about 5 min and maintained for between 45 and 90 min, depending on the operating pressure and hydrogen/hydrocarbon ratio.

A space time (defined as the volume of the reactor divided by the volumetric flow rate of the feedstream at reaction conditions) of 0.03 sec was used throughout most of this investigation for both reactor types. Hydrogen-naphtha feed molar ratios of 7.0 and 28 were used for the annular reactor and only a molar ratio of 28 was used for the open tubular reactor

The weights of gaseous products, pyrolysis gasoline and coke were determined as follows. The total weight of liquid feedstock was determine from the feed rate and total run time. The quantity of coke formed was determined from the difference in reactor weight before and after a run and the weight of non-condensable gas products was calculated by difference

RESULTS

Product distribution

Naphtha pyrolysis

Product yields (weight fraction of feed) obtained as a function of reactor temperature at a space time of 0.03 sec and a molar H_2/naphtha = 28 are shown in Table 2. The yields of the major gaseous products as functions of reactor temperature are also shown in Fig. 2. The reactor temperature was varied between 680 and 900°C and the ethylene yield increased monotonically from 0.20 to 0.60. Methane yield varied between 0.15 and 0.18 in this

TABLE 2

Product yields for naphtha pyrolysis for the annular reactor (S/V = 21.5 cm^{-1}; H_2/naphtha = 28)

	Product yields (wt. fraction of feed)					
	680°C	710°C	760°C	810°C	850°C	900°C
Methane	0.112	0.105	0.250	0.126	0.155	0.184
Ethane	0.030	0.040	—	—	—	0.046
Ethylene	0.197	0.320	0.362	0 435	0.528	0 601
Acetylene	0.017	0.003	—	—	0.002	0.001
Propylene	0.166	0.218	0.190	0.182	0.116	0.084
Propadiene	0.049	0.05	—	—	—	—
Butene-1	0.068	0.025	—	0.014	—	—
Butadiene	0.132	0.128	0.090	0.111	0 093	0 033
Butene-2	0.027	0 013	—	0.009	—	0.011
Isobutane	0.011	—	—	—	—	—
Coke	0.021	0.030	0.091	0.095	0.091	0.037

temperature range while propylene yield decreased from a high of 0.25 at 680° C to a low of 0.09 at 900° C. Butadiene yield dropped to 0.05 at 900° C.

Coke, gas, and pyrolysis gasoline yields are shown as functions of furnace temperature in Fig. 3. The most dramatic effect in this plot is the pronounced maximum in the coke yield at a reactor temperature of about 800° C. The

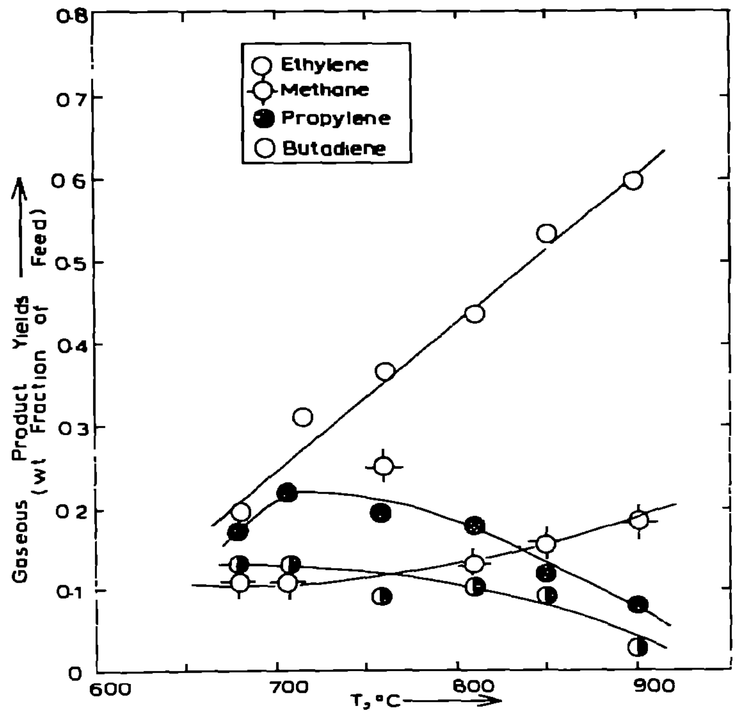

Fig 2 Major gaseous product yields vs temperature at H_2/naphtha = 28 and S/V = 21.5 cm^{-1}.

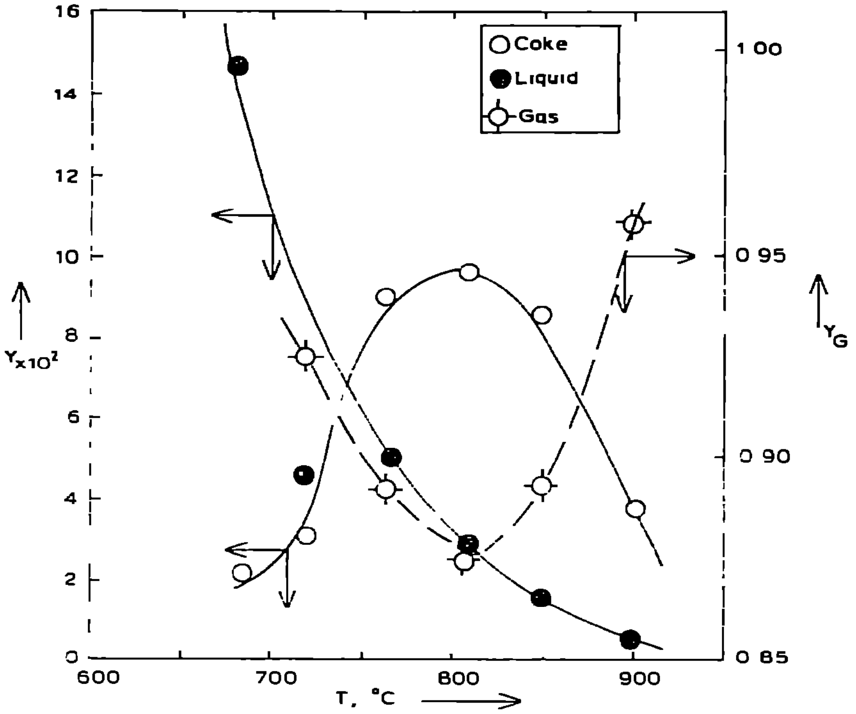

Fig. 3 Coke, gas and pyrolysis-gasoline yield vs. temperature at H_2/naphtha = 28 and $S/V = 21.5\ cm^{-1}$

total effluent gas yield went through a corresponding minimum as the coke yield went through a maximum but the pyrolysis gasoline yield decreases monotonically with increasing furnace temperature

The effect of CS_2 addition to the naphtha feed (mole fraction of CS_2 in the feedstream = 0.06) on ethylene and methane yields at 850° C is shown also in Fig. 2. Ethylene yield was substantially reduced from 0.53 to 0.38 with CS_2 addition, while the methane yield was increased from 0.15 to 0.34. The effect of CS_2 addition on coke, total gas an liquid yields is also shown in Fig. 3. The coke yield was decreased at this temperature from 0.09 to 0.06 with CS_2 addition due possibly to the passivity of the active metal surface by the formation of a metal sulfide. The corresponding total gas yield was increased from 0.89 to 0.93 while the pyrolysis gasoline yield was relatively unchanged with CS_2 addition.

Cyclohexane pyrolysis

Product yield for cyclohexane pyrolysis in the annular reactor at 750, 830 and 900° C, space time of 0.03 sec and hydrogen/cyclohexane ratio of 20 are shown in Table 3. The yields of the major gas products as functions of reactor temperature are also shown in Fig. 4. Compared to the product yields for naphtha pyrolysis, the following conclusions can be derived:

(i) ethylene yields was relatively insensitive to furnace temperature for cyclohexane pyrolysis, whereas it was observed to increase monotonically with temperature for naphtha pyrolysis;

TABLE 3

Product yields for cyclohexane pyrolysis for the annular reactor (S/V = 21 5 cm^{-1}; H_2/cyclohexane = 20)

	Product yields (wt fraction of feed)		
	750°C	830°C	900°C
Methane	0.168	0.142	0.124
Ethane	0 042	0.039	0.044
Ethylene	0.428	0.432	0.402
Propylene	0 087	0.146	0 041
Butene-1	0.012	0.016	0 015
Butadiene	0.151	0.132	0.264
Butene-2	0.014	—	—
Coke	0.097	0.098	0.105

(ii) propylene yield went through a maximum at a lower temperature for naphtha (~700°C) compared to cyclohexane (830°C);

(iii) butadiene yield increased from 0.15 at 750°C to 0.26 at 900°C for cyclohexane pyrolysis, while it decreased somewhat in this temperature range for naphtha pyrolysis from about 0.10 to 0.05.

Effect of S/V *and* H_2*/naphtha ratios*

Ethylene

Figure 5 shows the effect of hydrogen to naphtha ratio on ethylene yield in the annular reactor (S/V = 21 5 cm^{-1}). As shown clearly in this plot, the ethylene yield was strongly affected by a four-fold increase in the hydrogen

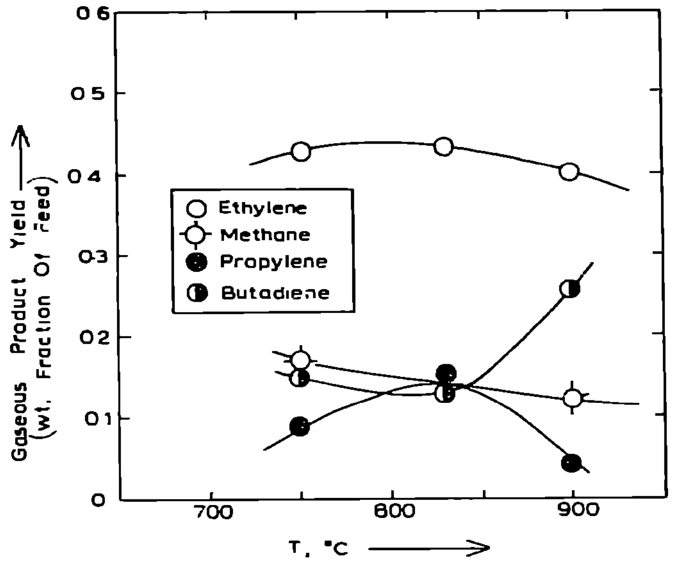

Fig. 4. Product yield vs temperature for cyclohexane pyrolysis (H_2/cyclohexane = 20, S/V = 21.5 cm^{-1}).

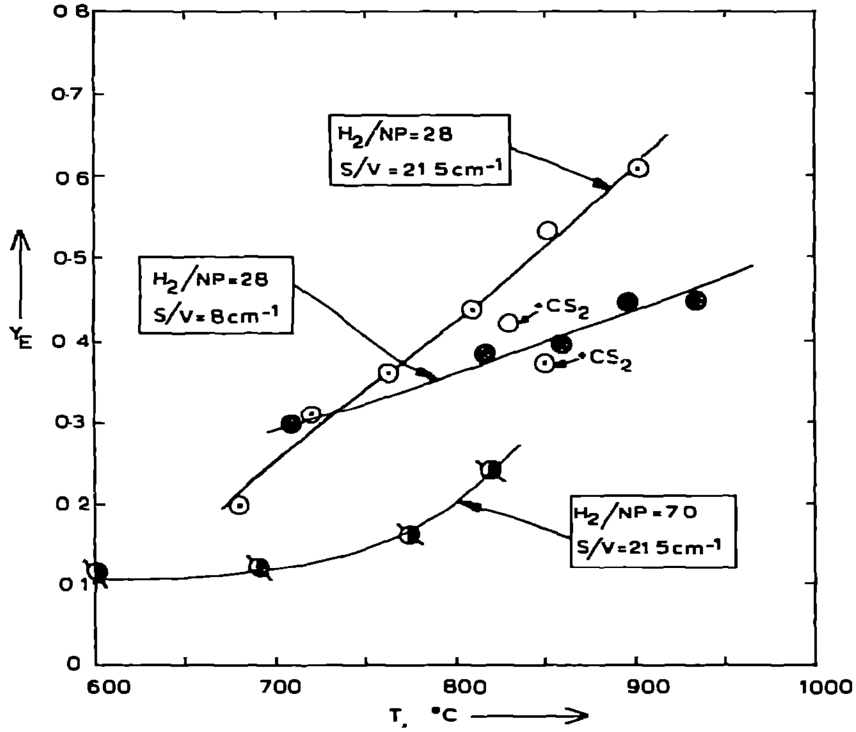

Fig 5 Ethylene yield vs. temperature for two H_2/naphtha ratios and two furnace tube sizes.

to naptha ratio as the lower ratio resulted in considerable decrease of the ethylene yield throughout the temperature range investigated. For example, at 775°C the ethylene yield at H_2/naphtha = 28 was 0.38 and this value was decreased to a value of 0.16 at a lower H_2/naphtha ratio of 7.0.

Also illustrated in Fig. 5 is the effect of tube size on ethylene yield at a constant H_2/naphtha ratio of 28. The larger tube size ($S/V = 8$ cm^{-1}) resulted in substantial decrease in ethylene yield when compared to the annular reactor ($S/V = 21.5$ cm^{-1}), especially at the higher furnace temperatures; for example, at 900°C the ethylene yield was decreased from 0.60 ($S/V = 21.5$ cm^{-1}) to 0.44 ($S/V = 8$ cm^{-1}).

The effect of CS_2 addition was also investigated on naphtha pyrolysis with the two tube sizes and the results are illustrated in Fig. 5. Ethylene yield resulting from CS_2 addition was closer to the general behaviour for the larger tube size.

Methane

Figure 6 illustrates the effect of tube sizes on methane yield. For a hydrogen: naphtha ratio of 28, the methane yield was found to be substantially lower for the annular reactor ($S/V = 21.5$ cm^{-1}). This is in contrast to what was observed for ethylene yield which was higher for the annular reactor. The scatter in the yield data for the four-fold increase in hydrogen to naphtha ratio makes it somewhat difficult to make a definite conclusion but there appeared to be no effect above 720°C. Again, CS_2 addition into

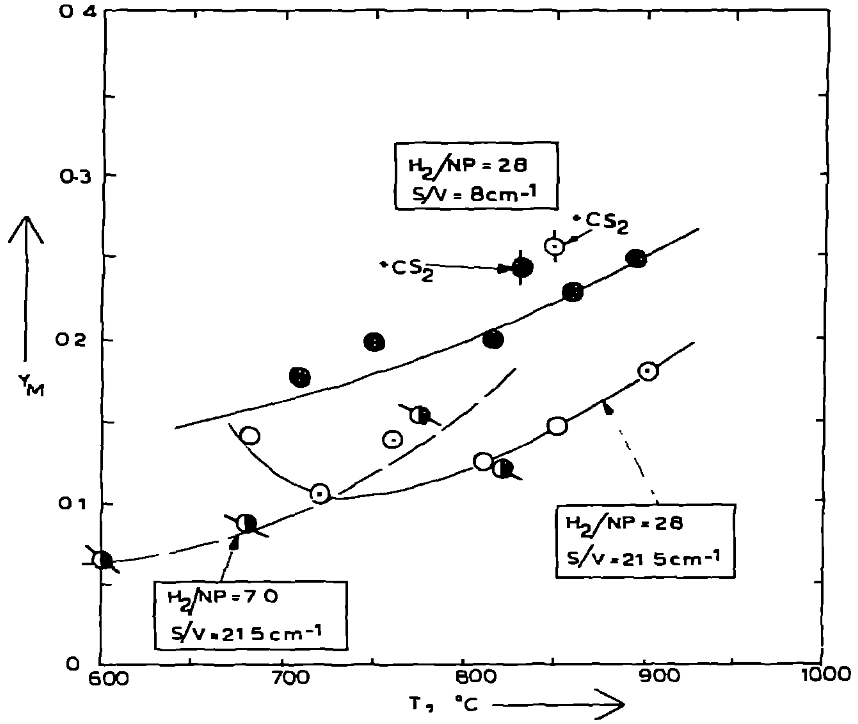

Fig. 6. Methane yield vs temperature for two H_2/naphtha ratios and two furnace tube sizes

either the annular and open tubular reactors was closer to the value for the larger reactor.

Coke

Figure 7 shows a comparison of the coke yield for various furnace temperatures at two hydrogen/naphtha ratios and two different tube sizes. The two curves for H_2/naphtha ratios of 28 and 7.0 (constant $S/V = 21.5 cm^{-1}$) show pronounced maxima as the furnace temperature was varied between 600 and 900°C. The maximum yield at H_2/naphtha = 7.0 was found to be 0.16 and the corresponding yield at H_2/naphtha = 28.0 was 0.098. In addition, the maximum coke yield was shifted to a higher temperature for the higher H_2/naphtha ratio. This temperature occurred sharply at 780°C for H_2/naphtha = 7.0 and a broad maximum occurred at about 800°C for H_2/naphtha = 28, representing a temperature shift of about 20°C

The effect of coke yield as a function of tube size was also investigated and is shown in Fig. 6. The coke yield was substantially decreased for the larger furnace tube, a strong indication of the effect of surface on the pyrolysis reaction. The coke yield behaviour for the larger reactor also exhibited a broad maximum and the coke yield was decreased by a factor of about 10 at the maximum as the surface to volume ratio was decreased by a factor of 2.7.

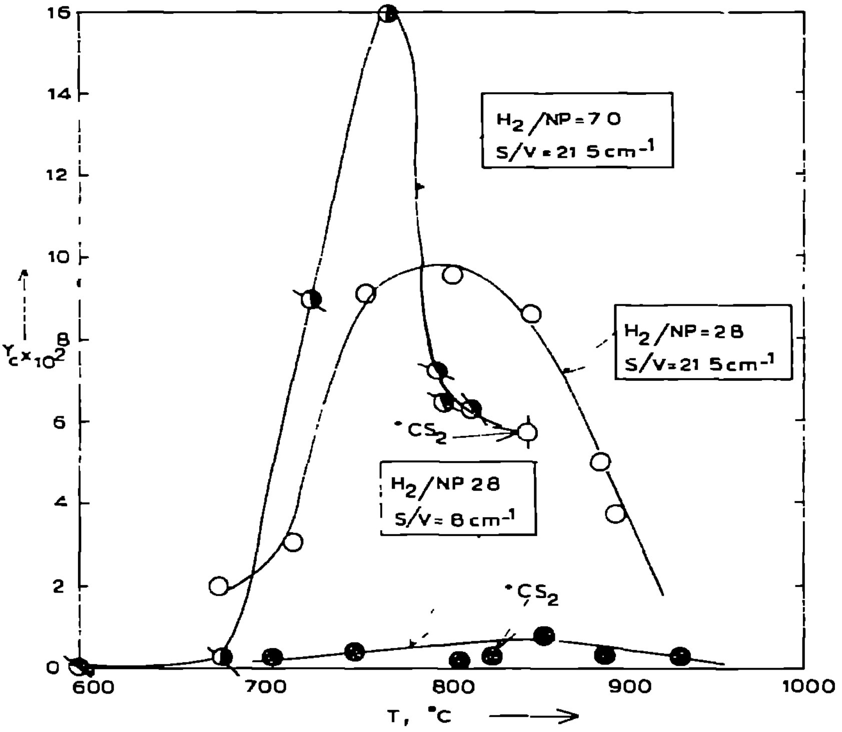

Fig. 7. Coke yield vs. temperature for two H_2/naphtha ratios and two furnace tube sizes.

DISCUSSION OF RESULTS

Ethylene

The results of this investigation clearly shows the beneficial effect of hydrogen on ethylene yield during pyrolysis of a naphthenic naphtha. The ethylene yield was found to increase monotonically with furnace temperature. The high ethylene yields resulted from the participation of hydrogen radicals in the pyrolysis reaction [12]. Enhanced ethylene yield was also observed previously for steam pyrolysis of naphtha and kerosene at the low residence time, high furnace temperatures and lower naphtha pressures used in this investigation [13,14].

The beneficial effect of hydrogen on heavy naphtha pyrolysis was reported previously [12] on a heavy Middle Eastern naphtha which was largely paraffinic with a PNA analysis of 60% paraffins, 25% naphthenes and 15% aromatics. A comparison of the product distribution obtained in this investigation with those of other workers is shown in Table 4 at furnace temperatures between 820 and 850°C. This comparison is not completely valid because the work reported here was done at a lower space time, compared to the work of Kunugi et al. [12]. This should result in higher ethylene yields as observed previously [13,14]. Nevertheless, the comparison of the two results is useful in highlighting the differences between ethylene yields during pyrolysis of paraffinic and naphthenic feedstocks with hydrogen dilution. Also shown in Table 4 are the results of a recent work on the pyrolysis of a Nigerian naphtha [5]. This work contained no informa-

TABLE 4

Comparison of pyrolysis of naphthenes with pyrolysis of paraffinic feedstocks

	Cyclohexane [a]	Nigerian [a] heavy naphtha	Nigerian [a] heavy naphtha	Nigerian [b] heavy naphtha	Middle-East [c] heavy naphtha
Cracking conditions					
Diluent	H_2	H_2	H_2	Not given	H_2
Diluent mole ratio	20	7.0	28.0		6 8
Residence time (sec.)	0.03	0.03	0 03		0.11
Temperature (°C)	830	820	850		850
Gaseous product yield (wt. fraction of feed)					
CH_4	0.142	0.118	0.155	0 195	0.163
C_2H_4	0 432	0 238	0.528	0 231	0.320
C_3H_6	0.146	0.098	0 116	10 32	0.109
C_4H_8	0 016	—	—	—	0 025
C_3H_6	0.132	0.103	0.093	0.088	0 033
Coke yield (wt. fraction of feed)	0 098	0 062	0 091	Not given	—
Hydrocarbon type analysis (% vol.)					
Paraffin	—	30.7	30.7	38.7	60
Naphthene	100	50.4	50.4	51 6	25
Aromatics	—	18.9	18.9	9 7	15
S/V (cm^{-1})	21.5 (ss) [d]	21.5 (ss) [d]	21 4 (ss) [d]	Not given	Quartz

[a] This work.
[b] Ref. 5
[c] Ref. 12.
[d] 304 stainless steel.

tion on reactor details, diluent type, coke and gas product variation with reaction conditions.

The ethylene yield at 820°C for a hydrogen dilution ratio of between 7—8 was 0.24 for a naphthenic naphtha compared to 0.32 for a paraffinic naphtha. It need be emphasized that the smaller space time used in this investigation favoured higher ethylene yield. At a higher diluent ratio of 28 for the naphthenic naphtha, the ethylene yield was 0.53 indicative of the increasing beneficial effect of higher hydrogen dilution on ethylene yield

A comparison of the pyrolysis of cyclohexane with a naphthenic naphtha can be made from the data presented in Table 4. At approximately the same cracking conditions, the ethylene yield was 0.47 for cyclohexane pyrolysis and 0.53 for naphtha pyrolysis. The higher ethylene yield for the naphtha is due to the accelerating effect of paraffins in naphthenic feeds [1].

The effect of surface on ethylene yield can now be summarized as follows.

(i) ethylene yield was lowered at temperatures above 730°C as the tube size was increased. Below 730°C where coke formation was low for both tube sizes, there was no significant difference in ethylene yield;

(ii) CS_2 addition into the annular reactor resulted in decreased ethylene and coke yields and correspondingly higher methane yield;

(iii) CS_2 addition to the larger diameter tube did not alter appreciably the previously observed yields for ethylene, coke and methane.

It can be concluded from these observations that as the furnace tube size was increased so as to minimize the effect of surface, both ethylene and coke yields were reduced while methane yield was increased. This is a puzzling observation because it is difficult to conjecture a surface-catalyzed decomposition reaction resulting in enhanced ethylene yield. Since propylene and butadiene were found to decrease with temperature, disproportionation reaction of the type

$$2C_3H_6 \rightleftharpoons C_2H_4 + C_4H_8$$

can be ruled out as these reactions are catalyzed by oxides or sulfides of molybdenum, tungsten and rhenium. Possible homogeneous reactions include concerted reactions of the type

$$2\ C_3H_6 \rightleftharpoons 3\ C_2H_4$$

and secondary reactions promoted by hydrogen [15] of the type

$$C_3H_6 + H_2 \rightleftharpoons CH_4 + C_2H_4$$

should occur at the same rate for identical reactions conditions, irrespective of tube size. However, these reactions may account for the observed increase of ethylene at high temperatures where secondary decomposition reactions become significant [16].

Coke

A strong effect of surface on coke yield was observed and this was attributed to the catalytic effect of iron, nickel and possibly chronium present in 304 stainless steel used in this investigation. Nickel has been shown to be the most active of the three metals [17] and the order of decomposition has been shown to be acetylene > olefins > paraffins. For the olefins, the rate of coke formation is highest for ethylene and the C_3—C_4 olefins require minimum ratios of hydrogen/olefin for the decomposition to occur [17—19]. Consequently, the observed coke effect in this work must be attributed tc the presence of nickel in stainless steel and all of the olefins present in the pyrolysis tube should undergo destructive decomposition to coke.

The maximum in the coke yield and rate of coke formation observed in this investigation at temperatures between 780 and 800°C depending on the ratio of hydrogen/naphtha has been observed previously on nickel and iron, although at lower temperatures of ~550°C The shift in $T_{\max}$ with increasing ratio of hydrogen/hydrocarbon was also observed for propylene—hydrogen decomposition on nickel [19] and CO—hydrogen on iron [20]. These studies did show a minimum in the rate of coke formation at 600°C and then a sharp rise in the rate as the temperature rose above 600°C. This general trend is in agreement with the results of this investigation because low coke yield or rate of coke production was observed at ~600°C and the coke rate then increased. The maximum coke rate observed here at ~780—800°C has not

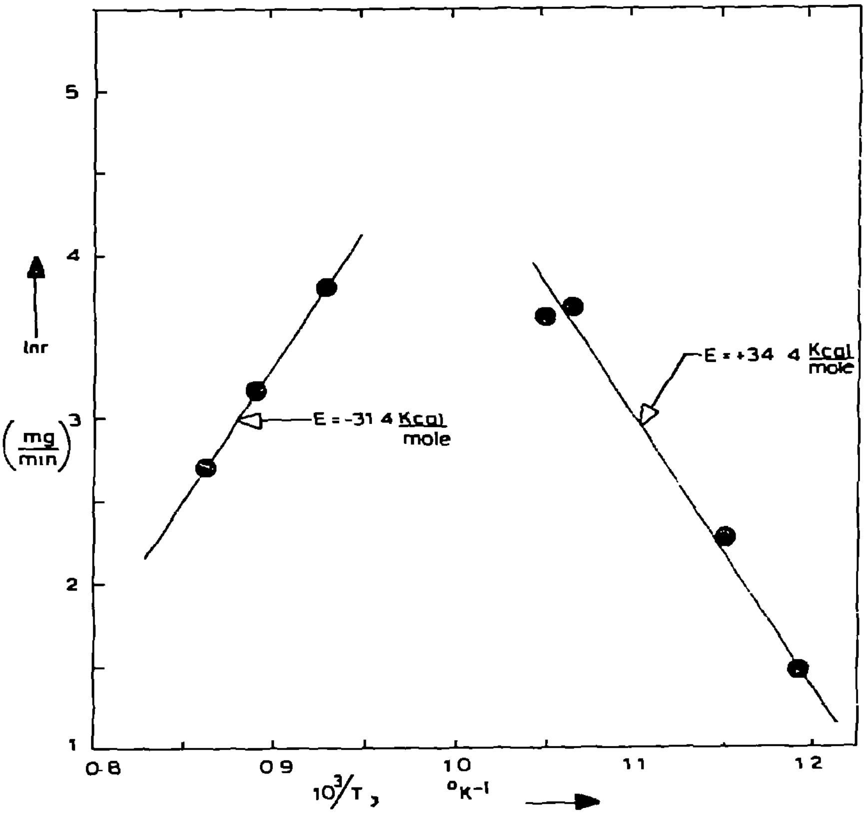

Fig. 8 Arrhenius plot of the rate of coke deposition vs $1/T$ (H_2/naphtha = 28, S/V = 21 5 cm^{-1}).

been previously reported. Walter et al. [20] showed that the crystalline character of carbon deposited from CO—H_2 decomposition on iron increased with increasing temperature of formation to a maximum and then decreased with further rise in temperature. Recrystallization of carbon catalyzed by nickel has also been observed at temperature of ~1000°C [21]. This literature observations together with our result strongly suggest multiple maxima for metal-catalyzed coke formation as temperature is increased.

Various suggestions have been made regarding the mechanism of carbon deposition on metals, the most recent by Bernardo and Lobo [18]. Catalyst sintering above T_{max} can be rejected as the explanation for the maximum because as observed previously [17], the process was reversible. It is generally agreed that the region preceding T_{max} was diffusion controlled with activation energies between 29—34 kcal $gmole^{-1}$ in agreement with published values of the energy of diffusion of carbon through nickel. An Arrhenius plot of the data obtained in this investigation (see Fig. 8) resulted in activation energies of +34.4 kcal $mole^{-1}$ and —31.4 kcal $mole^{-1}$ for regions before and after T_{max}, respectively. The mechanism for coke formation in the region below T_{max} may be limited by carbon diffusion. The mechanism for coke formation in the region above T_{max} has been attributed to decreasing adsorption and surface kinetic control resulting in negative value of the activation energy [17]. This diffusion and surface controlled mechanism of metal catalyzed olefin decomposition to coke probably reoccurs at the higher temperatures of this investigation.

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