

Figure 1 Plots of different types of hydrogen versus measured smoke point (SP) for different kerosene fractions: ●,  $H_{dar}$ ; ×,  $H_{mar}$ ; □,  $H_x$ ; △,  $H_\beta$ ; +,  $H_\gamma$ .

The smoke point of all the samples was determined according to the standard method<sup>11</sup>. The data were processed by computer using a multiple regression analysis program.

### RESULTS AND DISCUSSION

The broad cut kerosene fractions (140–275°C) were taken from crudes of different Indian origin. To make the study independent of variation in the kerosene boiling range, various sub-fractions were also included in the correlation development. The smoke point (SP) of kerosene fractions varied from 14 to 27. Table 1 shows the different hydrogen type regions of the <sup>1</sup>H n.m.r. spectra used to obtain different hydrogen type distributions. To know the trend of variation of different types of hydrogen with smoke point, the content of hydrogen types were plotted against smoke point for a few typical broad cut kerosenes, and are presented in Figure 1. The effect on the smoke point of  $H_{dar}$  seems to be relatively greater as compared with  $H_{mar}$ , supporting the fact that naphthalene content of a kerosene/jet fuel applies a secondary control upon its combustion characteristics. The results were also checked for their linear correlation with smoke point.  $H_{dar}$ ,  $H_x$  and  $H_\gamma$  showed a relatively higher correlation coefficient as compared with  $H_\beta$  and  $H_{mar}$  when correlated individually. Based on these trends (Figure 1), attempts were made to correlate the smoke point with a linear combination of hydrogen types which yielded statistically poor results. Hence the relation between smoke point and hydrogen types was taken in the form:

$$SP = A_0 + A_1(1/H_{mar}) + A_2(1/H_{mar}^2) + A_3(H_{dar})^{1.5} + A_4(H_{mar})^{0.5} + A_5(H_x) + A_6(H_\beta/2)^{0.5} + A_7(H_\beta/2) + A_8(H_\gamma) + A_9(H_\gamma)^{0.5} \quad (1)$$

where  $A_i$  are the hydrogen type compositions normalized to unity. Attempts<sup>2</sup> to reduce the number of constants in Equation (1) were made, and it was found that the best correlation was obtained when the number of constants were reduced to 10. Further reduction of the number of constants reduced the correlation coefficient drastically (from 0.9711 to 0.8944). Hence the above equation was found to be statistically satisfactory. The values for  $A_i$  and the measures of the correlation are listed in Table 2. Lower values of  $A_3$ ,  $A_5$  and  $A_8$  show that the hydrogen types that have dominant effects on the combustion quality of kerosene fuels are  $H_{dar}$ ,  $H_x$  and  $H_\gamma$ . Smoke formation is characterized as the formation of soot or hydrogen-deficient condensed structures that are not completely burnt to  $CO_2$  and water vapour under combustion conditions.  $H_{dar}$  qualitatively predicts the condensed structures in the kerosene sample, while  $H_x$  represents the substituents on the aromatic rings (mono- as well as di-aromatics). These substituted positions during combustion become active points due to cleavage of alkyl groups. They facilitate condensation, which in turn produces larger amounts of soot and/or condensed structures<sup>9</sup>.  $H_\gamma$  measures the branching in the paraffins and/or in the alkyl chains attached to aromatic rings, and it is established<sup>8</sup> that such branching acting as an oxidation retardant, shows a marked decrease in the smoke point.

Cookson *et al.*<sup>4</sup> found that no significant advantage was gained when the aromatics were divided into the three parameter model, but in the present work a relatively greater influence of  $H_{dar}$  as compared with  $H_{mar}$  was observed. A high value for  $R^2$ , the coefficient of multiple regression, of 0.9711 is associated with a standard deviation of 0.891 mm, which compares better with the 2mm repeatability specified in the standard test procedure for smoke point measurement<sup>11</sup>. Smoke points of different kerosene samples predicted by the proposed equation are plotted against the measured values in Figure 2.

Table 2 Measures of correlation and constants

Standard deviation of residuals	0.891
Correlation coefficient	0.971
Constants:	
$A_0$	313.93
$A_1$	-1168.09
$A_2$	1308.30
$A_3$	-1.29
$A_4$	116.53
$A_5$	-0.82
$A_6$	168.99
$A_7$	-14.36
$A_8$	7.18
$A_9$	-97.95

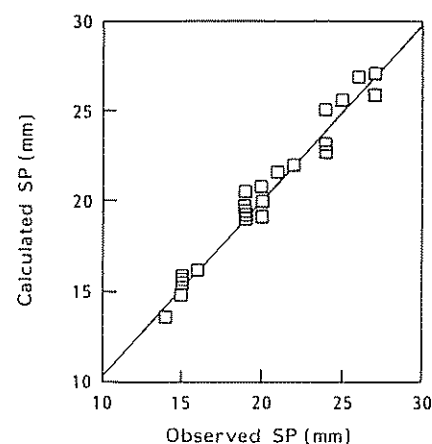


Figure 2 Plot of measured smoke point (SP) values for different kerosene fractions versus those calculated from Equation (1) using the coefficients in Table 2

### CONCLUSIONS

Smoke point has been correlated with kerosene chemical structure, which is obtained on the basis of <sup>1</sup>H-n.m.r. spectrometry. The developed method is fast, accurate (the standard deviation being 0.891 mm), and requires very small quantities of sample as compared with the standard IP method. The method is applicable to any kerosene sample boiling within the range 140–275°C. The applicability of the proposed correlation to either straight run kerosene other than Indian or the cracked kerosenes has not been checked.

### ACKNOWLEDGEMENTS

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## Gasification induced densification of form coke

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Shrinkage of form coke during its gasification in CO<sub>2</sub> in the kinetically limited regime (zone 1) is found. This shrinkage is attributed to preferential gasification of crosslinks between small, poorly aligned carbon crystallites, thereby allowing their improved alignment to proceed during gasification.

(Keywords: gasification; coke; carbon dioxide)

Recently, Hurt *et al.*<sup>1</sup> reported that kinetically limited gasification of chars does not occur at constant particle diameter, as is widely assumed, but is accompanied by gasification-induced particle shrinkage. The chars were prepared by slowly heating the precursor coals in 0.1 MPa N<sub>2</sub> to 1000°C and holding for 1 h. Char gasification was performed in 0.1 MPa air at 400–600°C. The gasification reaction, by breaking bonds, removing cross links, and removing carbon atoms, may facilitate densification via atomic rearrangements analogous to those occurring spontaneously at somewhat higher temperatures.

We have studied the gasification of form coke in CO<sub>2</sub> between 700 and 850°C in the kinetic, zone I region<sup>2</sup>, and also find that the coke undergoes significant shrinkage during gasification. This shrinkage reduces the extent of the decrease in coke density that is expected to occur as a result of gasification in zone I. Mechanical properties of form coke, such as Young's elastic modulus, fracture toughness, and fracture surface energies, are known to be strongly dependent upon coke density<sup>3</sup>, so any phenomenon that minimizes the decrease in coke density during its burn-off is of interest. Coke shrinkage during gasification will enhance the mechanical behaviour of cokes when used in the blast furnace. Our studies are briefly summarized in this communication.

## EXPERIMENTAL

The coal used in the preparation of the form cokes was Illinois No. 6 HVC bituminous. The dried coal was crushed to < 3.2 mm in size, pre-oxidized at 180°C to remove its caking characteristics, and then heated to 500°C in an O<sub>2</sub>/steam environment to separate the tar and char fractions. The char was then calcined at 815°C, liberating some volatiles and causing some particle shrinkage. The tar

was processed by introducing air at 100°C to yield a pitch. Forty parts by weight pitch were mixed with 60 parts by weight char; the mixture was heated to 85°C and moulded into rectangular bars 127 × 25 × 13 mm in thickness. The bars were heated in an inert atmosphere at 11°C min<sup>-1</sup> up to 870°C, and held for 20 min. Rectangular bars were used in this study to facilitate mechanical property measurements<sup>3</sup>, although form coke is normally moulded into a pillow-shape.

Prior to gasification studies, specimens 12.5 mm in width, 70 mm in length and 12.5 mm in thickness were prepared from the larger bars. Six specimens were reacted in flowing 0.1 MPa CO<sub>2</sub> or CO/CO<sub>2</sub> mixtures for varying lengths of time at 700–850°C. At intervals, they were removed from the furnace and weighed, to obtain a weight loss-time reactivity plot. Prior to reaction, the specimens were heated in 0.1 MPa N<sub>2</sub> to reaction temperature and held for two 5 h periods, after which they were removed from the furnace and weighed and measured.

## RESULTS AND DISCUSSION

Table 1 presents selected physical properties for the form coke. Bulk densities were measured on 123 bars. The other properties were measured on samples having an average bulk density of 0.83 g cm<sup>-3</sup>. The form coke has a large open porosity and surface area, and low bulk and true densities. This is consistent with the form coke being composed of small, poorly aligned crystallites, with crosslinking between crystallites, thus

Table 1 Physical properties of form coke

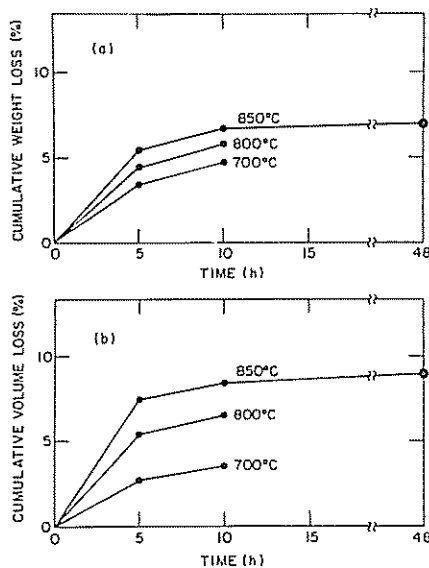
Property	Value
Bulk density range	0.70–0.94 g cm <sup>-3</sup>
Average bulk density	0.83 g cm <sup>-3</sup>
X-ray (true) density	2.07 g cm <sup>-3</sup>
Surface area (CO <sub>2</sub> , 298 K)	475 m <sup>2</sup> g <sup>-1</sup>
Fractional porosity (open to H <sub>2</sub> O)	0.497

possessing a large, open porosity and surface area in micropores.

Figure 1 shows the effect of pretreatment of form coke in N<sub>2</sub> on weight loss and volume change. Prior to heat treatment, specimens were dried at 120°C in air for 6 h to remove physically adsorbed water. Weight loss is due to removal of chemisorbed oxygen as CO and CO<sub>2</sub> (Ref. 4). Weight loss is accompanied by a significant volume loss at all heat treatment temperatures. Essentially, both losses are complete after 10 h soak time. Reactivity plots (weight loss versus time) for the gasification of form coke in CO<sub>2</sub> were essentially linear, having rates of 0.07, 0.59, and 1.52 wt% h<sup>-1</sup> at temperatures of 700, 800, and 850°C, respectively. As discussed by Walker *et al.*<sup>2</sup> the dimensionless parameter

$$\varphi^2 \eta = \frac{R}{C_R D_{\text{eff}}} \left( \frac{dw}{dt} \right) \quad (1)$$

where  $R$  is specimen thickness,  $C_R$  is CO<sub>2</sub> concentration,  $D_{\text{eff}}$  is effective diffusion rate of CO<sub>2</sub> into the form coke, and  $dw/dt$

Figure 1 Effect of pretreatment in N<sub>2</sub> on weight and volume loss of form coke

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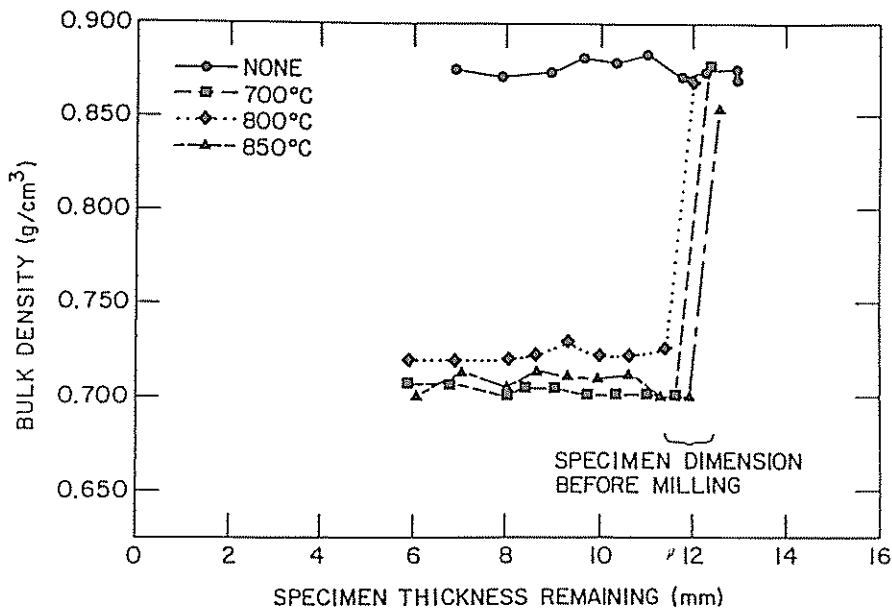


Figure 2 Bulk density profiles of form coke before and after gasification in  $\text{CO}_2$

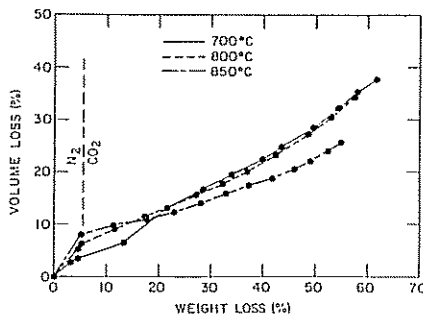


Figure 3 Volume loss of form coke during gasification in  $\text{CO}_2$

is gasification rate, can be used to determine the reaction zone in which gasification is occurring. For values of  $\varphi^2\eta < 0.1$ , reaction occurs in zone I in the kinetic limited regime. As calculated elsewhere<sup>5</sup>,  $\varphi^2\eta = 0.04$  for gasification at  $850^\circ\text{C}$ . Thus, reaction at this temperature and below occurred in zone I in this study.

As discussed elsewhere<sup>2</sup>, if gasification is described by zone I kinetics, it is expected that: reaction is uniform through the specimens; and no decrease in the external dimensions of the sample occurs. Adherence to the first condition requires that the bulk density through the sample is uniform following gasification. Figure 2 presents bulk density profiles through form coke specimens before and after gasification at different temperatures to  $\approx 40\%$  weight loss. Density profiles were measured by removing known thicknesses of form coke using a lathe, then obtaining the weight of the specimen remaining. It was not possible to

characterize samples  $< 6$  mm in thickness, due to the friability of the sample. Bulk densities through the samples were essentially uniform prior to and following form coke gasification, meeting one of the requirements of zone I kinetics. Bulk density decreased from  $\approx 0.87 \text{ g cm}^{-3}$  for the original form coke (prior to pretreatment in  $\text{N}_2$  and gasification in  $\text{CO}_2$ ) to  $\approx 0.71 \text{ g cm}^{-3}$  following gasification. However, if the external volume of the form coke had not changed during heat treatment and gasification, the

final bulk density should have been  $\approx 0.52 \text{ g cm}^{-3}$ . In fact, even though reaction occurred uniformly through the sample during its gasification, loss in volume also occurred concurrently and continuously, as seen in Figure 3.

Figure 4 shows that gasification of the form coke to  $\approx 40\%$  weight loss produced a major decrease in its Young's elastic modulus, from  $\approx 15$  to  $\approx 5$  GPa. However, in the absence of form coke shrinkage during gasification, Young's elastic modulus would have been reduced still further, to  $\approx 3$  GPa, according to the experimental correlation found between Young's modulus and coke density<sup>3,5</sup>.

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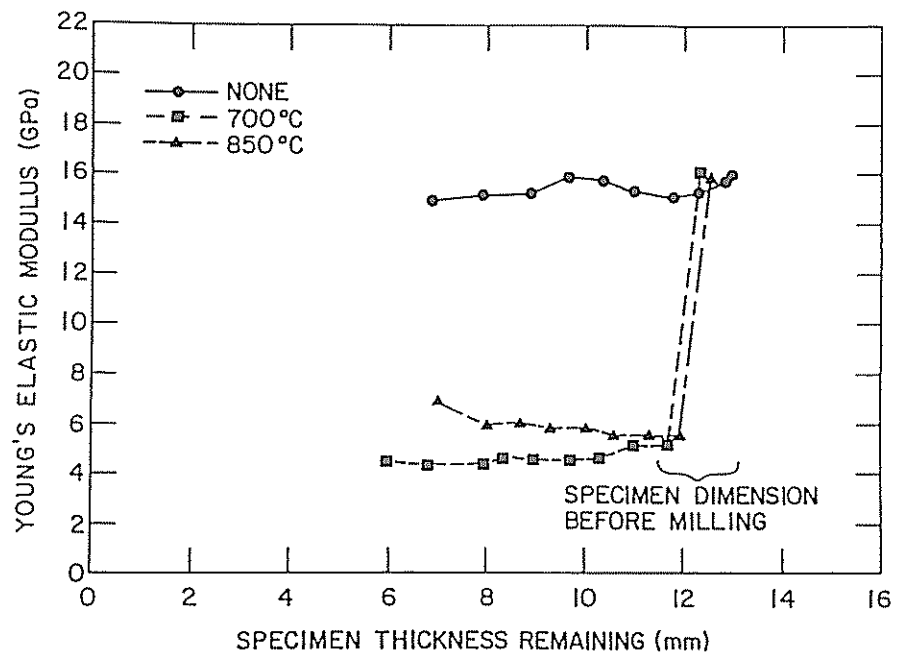


Figure 4 Elastic modulus profiles of form coke before and after gasification in  $\text{CO}_2$

## Deparaffination of light crudes through urea-n-alkane channel complexes

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Solid urea-n-alkane channel complexes were obtained by reacting urea with calculated amounts of three crude oils (Qua Iboe Light (QIL), Trans Niger Pipeline (TNP), and Brass Blend (BB)) from different Nigerian wells. A fourth Nigerian crude, Bonny Light (BL), gave no adduct with urea under the same conditions. Decomposition of the complexes gave n-paraffins whose weight distributions were analysed by gas chromatography. BB gave n-paraffins of homologous series from C<sub>7</sub> to C<sub>34</sub>, while those from QIL and TNP each ranged from C<sub>9</sub> to C<sub>34</sub>. Calculation of ratios of odd to even carbon numbers showed a slight predominance of odd-numbered n-paraffins. Experimental data also suggest that BB, QIL and TNP are of the same stratigraphic horizon and geographical region, but different from BL.

(Keywords: crude oil; gas chromatography; cracking)

The use to which a particular crude oil is put depends on its inherent characteristics, which also influence the fine details of refining processes, such as cracking or reformation. One such inherent characteristic is the n-alkane content. n-Alkanes are known to be present in virtually all crudes and in many of their distillation fractions, and consequently they influence the properties of most of the products derived from crude oil. Depending on the chain lengths, n-paraffins are used commercially as solvents<sup>1</sup>, in making linear alkyl-benzenes which serve as precursors for the manufacture of soaps and synthetic detergents<sup>1,2</sup>, and in the production of plasticizers<sup>1,2</sup> and single cell protein<sup>1-3</sup>. n-Paraffins can also serve as precursors for long chain fatty acids. C<sub>10</sub>-C<sub>18</sub> acids are esterified to yield edible fats, while the sodium soaps of C<sub>18</sub>-C<sub>25</sub> acids are used as lubricating greases.

From a commercial standpoint, urea remains one of the best complexing agents for n-paraffins, since it is selective, inexpensive and forms well-defined filterable channel complexes<sup>4-7</sup>. In the presence of n-alkanes, the tetragonal crystal structure of urea rearranges and becomes loosely coiled around the straight-chain hydrocarbon in a hexagonal spiral<sup>4,7</sup>. The channel formed by this spiral varies in width between about 5 and 6 Å, and can thus form inclusion complexes with n-paraffins, which have a cross section<sup>7</sup> of about 4.1 Å.

Channel complexes formed by urea and n-alkanes have attracted world-wide attention during the past four decades, and a voluminous literature is available on experimental techniques and on the structures, properties and applications of both the complexes and the extracted n-alkanes<sup>7-10</sup>. Such studies have not hitherto been extended to Nigeria's vast crude oil reserves, which enjoy considerable status in international markets as sweet crudes, and qualitative and quantitative information on the n-

paraffin contents of these crudes is lacking.

## EXPERIMENTAL

## Reagents and materials

Urea (Aldrich) and the solvents CH<sub>3</sub>OH (B.D.H.), CH<sub>2</sub>Cl<sub>2</sub> (B.D.H.) and C<sub>6</sub>H<sub>6</sub> (Aldrich) were of analytical grade and were used without further purification. The de-watered crude oil samples Brass Blend (BB), Qua Iboe Light (QIL), Trans Niger Pipeline (TNP) and Bonny Light (BL), were supplied by the Nigerian National Petroleum Corporation (R. & D.) Port Harcourt, Nigeria. The viscosities of the crude oil samples and those of dilutions were determined at 30°C (ambient temperature), and densities were taken with hydrometers.

## General urea-adduction procedure

The crude oil (100 ml) was diluted with a calculated volume of CH<sub>2</sub>Cl<sub>2</sub> to obtain a viscosity of 1.5 mm<sup>2</sup> s<sup>-1</sup>. This diluted sample was mixed at room temperature (30°C) with an equal weight of urea activated with 4% aqueous CH<sub>3</sub>OH. The mixture was stirred for 60 min at 1400 r.p.m., and filtered at the pump. The residue, solid urea-n-alkane adduct, was washed with benzene (100 ml) and then decomposed with water (exothermic) in a separatory funnel to give semi-

solid/solid n-alkanes (upper layer) and an aqueous (lower) layer. Further washing of the n-alkanes layer with water ensured the complete removal of urea. To remove any traces of water, the n-alkanes were melted, kept at ≈75°C, and mixed with 1 g of anhydrous granular (≈782 μm) CaCl<sub>2</sub>. The hot mixture was then centrifuged at 2000 r.p.m. for 3 min to separate the n-alkanes from the CaCl<sub>2</sub>.x H<sub>2</sub>O precipitate. The decanted hydrocarbon was cooled and weighed (Table 1) before being subjected to g.c. and i.r. analyses.

## Infrared spectra

Spectra were obtained using undiluted samples as films on KBr discs. The results for the four crude oil samples and for the corresponding n-alkanes are shown in Table 2, where absorption band intensities are classified as very strong (vs), strong (s), medium (m), weak (w) or very weak (vw); only those bands classified as 'w' or stronger for at least one of the samples are included.

## Gas chromatography

Gas chromatograms of the n-paraffins were recorded with an instrument fitted with a flame ionization detector and a stainless steel column 10 ft long × 1/8 in. i.d., packed with 10% sp-2100 liquid phase on chromosorb WHP support

Table 1 Reaction conditions<sup>a</sup> and results

Crude oil	$d_{30}^0$ (g cm <sup>-3</sup> )	Wt. of urea (g)	Wt. of adduct (g)	Yield of n-alkanes	
				(g)	(%) <sup>b</sup>
BB	0.807	81.20	94.15	11.96	15
QIL	0.830	82.94	110.76	26.09	31
TNP	0.835	83.55	116.95	32.84	39
BL	0.885	87.96	nil	nil	-

<sup>a</sup> 100 cm<sup>3</sup> reacted for 60 min; see Experimental section<sup>b</sup> Based on weight of crude used