Boiling range distribution characteristics of coal-derived liquids by simulated gas chromatographic distillation technique

Prem S.M.Tripathi[1]*, Sadhan K.Chakraborty[1], Dilip Thakur[2], R.C.Tripathi[1]

[1]Central Institute of Mining and Fuel Research(CIMFR)-Digwadih Campus, 403,
Mamta Shubham Apartments, Jai Prakash Nagar, Dhanbad-826001, Jharkhand, (INDIA)
[2]STIIT, Baramore, Gwalior, M.P., (INDIA)
E-mail : psmtripathi@yahoo.com; psmtripathi45@gmail.com; wavemail@rediff.com

ABSTRACT

Gas Chromatographic Distillation (GCD) technique, based on ASTM D-2887 method, has been employed for studying the boiling range distribution characteristics of the kerosene fraction (150-250°C) and of upgraded coal-hydogenates. Through this study, the suitability of ASTM D-2887 method as a substitute of ASTM D-286 has been established for the characterization of coal-hydogenates, derived from a bituminous Indian coal, namely, Raniganj coal [Raniganj coalfields, (W.B.) of Eastern Coalfields Ltd,,]. Reported in the present study are the results of characterization of three upgraded coal hydrogenates (150-250°C), and also a low-boiling (IBP-180°C) primary coal-hydogenate, for which GCD technique has been advantageously exploited. The results thus clearly suggest that the ASTM D2887 – based GCD technique is a useful and superior analytical method for the precise characterization of boiling fractions of the kerosene fraction (150-250°C) of upgraded coal-hydogenates and that the analytical data may well prove useful for the selection of catalyst for the liquefaction of coals and their subsequent upgradation effectively. The GCD analytical data is also useful for the product yield calculations, material balance, and also for understanding the correlation between the physical properties of the products in different boiling range of the coal-derived hydrogenates.
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KEYWORDS

INTRODUCTION

Limited availability of our oil reserves, coupled with Machiavellianism of Oil Producing and Exporting Countries (OPEC) in arbitrarily deciding to increase the price of crude oil, and in the absence of easy and abundant availability of commercially exploitable alternative sources of energy in a foreseeable future, the need for clean and environment-friendly production of synthetic oil from coal via direct coal hydrogenation and/or gasification route (Fischer-Tropsch synthesis) has, especially for India, become more relevant and imperative today and cannot be but over emphasized. Therefore, simultaneous efforts are on for development of both ''green'' coal technologies, and bio-fuels, as also renewable sources of energy (solar, wind, hydrothermal,

geothermal, tidal wave etc.), *in tandem* with recent renewed tempestuous vigor to harness nuclear energy. Nonetheless, till these alternative energy sources are fully developed and are abundantly available for commercial exploitation, the predominant dependence of coal in India for power generation and other industries shall continue for coming several decades.

One of the proven routes for the production of "synthetic oil" from coal is the famous Bergius or, more commonly, "coal hydrogenation" process, which, defined simply, is the process of converting powdered coal mixed with tar to oil by making carbon in the coal combine with hydrogen at a temperature of 450°C under pressure (200 atmospheres) in the presence of a catalyst to form oil (mixture of hydrocarbons for fuel)[1a,b] During this coal hydrogenation process, many fractions in different boiling range (hydrogenates)-similar to petroleum fractions, are obtained, after fractionating and refining of which different types of fuel (petrol, diesel, ATF, etc.) are produced[1c]. As such, characterization of different boiling range hydrogenates is necessary.

Over the past four decades or so, gas chromatography (GC) has played a most important role in the analysis of oil. Moreover, with the constant advancements in the technique, especially with the introduction and decisive role of capillary GC, the use of selective detection techniques, the versatility of coupled-column techniques and, specifically, the additional power of comprehensive two-dimensional GC and computer-assisted data analysis, it has acquired a unique position and has irrefutably become the analytical chemists' forte, particularly for the analysis and characterization of different components in liquid and gaseous mixtures and most importantly, crude oil distillation fractions, petroleum products and petrochemicals and has been logically extended to synthetic oil obtained by coal hydrogenation. The boiling range distribution of liquid hydrocarbons in synthetic fuels, like coal-derived fuels, is a very important and significant characteristic as it is used to evaluate many operational data, e.g. yield calculations, material balance, correlation of some physical properties, and even for computer simulation operations. For the determination of the boiling range distribution in coal hydrogenation -derived hydrocarbons, such distillation techniques as ASTM D-86[1], ASTM D1160[2], and

Japanese Industrial Standard, JIS-K2254[3] have earlier been made use of. However, these methods suffer from certain limitations in that they are time consuming and require large amount of samples (minimum 100 ml), because of which the need for development of newer, efficient, less time consuming, and less sample (1 ml or so) requiring technique was felt. Subsequently, with the advent of simulated distillation by gas chromatography, which, over the years, came to be known as Simulated Gas Chromatography Distillation (SGCD) technique and designated as ASTM D2887[4], the aforesaid limitations were overcome and gradually it came in vogue and found wide acceptance. Thus, simulated gas chromatography distillation technique is an analytical method which advantageously replaces traditional distillation methods for rapid checking of petroleum products yields. In this technique, the choice of the stationary phase is very important so as to obtain good agreement with the real distillation curves. Also, this phase should be stable at the maximum temperatures used. This improved technique, besides being fast, accrate, and reliable, requires relatively a much lesser time of analysis, and a very small quantity (0.2 μl) of sample. The arrival in the last few years of very stable metal capillary columns has provided better control of the experimental parameters involved in these two problems. With these columns the determined final boiling point of simulated distillation methods has been extended and some procedures have been defined to use these methods in routine analysis. Results of simulated distillation are in good agreement with the physical distillation. Automation of these methods has become feasible in recent years by developing software which carries out the raw data processing rapidly, the calculation of the SD curve, and controls all parameters of the defined procedure. All these attractive features have made the simulated GCD technique a reliable, versatile, fast, sensitive, and accurate analytical tool, especially for precisely ascertaining the boiling range distribution characteristics of complex liquid mixture samples like various petroleum fractions. The suitability of the GCD technique has been advocated and reported by Kiser and Malore[1], while comparing the simulated distillation data with T.B.P. distillation data of H-coal distillates. In yet another study, Yoshida et al.[6] have also reported the applicability and superiority of the GCD technique for the characteriza-

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tion of upgraded liquid fuel obtained from the hydrogenation of a Japanese coal, viz., Teiheiyo coal. The principles, systems, as also wide ranging applications of GCD technique for the studying the boiling range distribution characteristics of crude oil and different petroleum fractions comprising mixture of complex compounds, primarily of hydrocarbons have been reported by several investigators[7-16].

At Central Institute of Mining and Fuel Research (CIMFR), Dhanbad (India), simulated GCD technique has advantageously been made use of for characterizing a wide variety of gas and liquid samples of coal-derived products. The present paper seeks to appraise the adaptability of ASTM 2887-based GCD or SGCD technique for the characterization of boiling range distribution of upgraded coal hydrogenates. The analytical results of GSD characterization of the kerosene fraction (150-250°C) and of upgraded coal-derived liquids obtained from the hydrogenation of a bituminous Indian coal, viz. Raniganj coal (Eastern Coalfield Ltd.) are reported hereinunder.

EXPERIMENTAL

Selection of coal

As mentioned above, the coal selected for this study was a bituminous, non-coking coal from Raniganj coal mines of Eastern Coalfield Ltd. The proximate and ultimate analyses of this coal are given in TABLE 1 below:

The coal sample for hydrogenation experiments was prepared by crushing the coal lumps to fine powder by quartering and coning method.

Preparation of primary and upgraded coal-hydrogenates

The non-catalytic primary and catalytically upgraded (in the presences of Ni-Mo, Ni-W, and Co-Mo commercial catalysts) coal hydrogenates were obtained by batch-wise direct hydrogenation of the powdered Raniganj coal admixed with tar at a temperature of 400°C in an Autoclave in the Coal-hydrogenation Laboratory of the Synthetic Fuel Division of the erstwhile CFRI (now CIMFR-Digwadih Campus), Dhanbad. The boiling range distribution characteristics of the hydrogenates thus obtained were studied by SGCD technique.

Gas chromatograph

The gas chromatographs used in the present work were Perkin-Elmer Auto System XLGC (US make, Model ASXL-610 N), and Perkin-Elmer GC, model 3920 B).

Experimental details of simulated gas chromatographic distillation (SG-DC) method for coal-derived liquids (hydrogenates)

Before recording the gas chromatographic distillation chromatograms of the coal-derived liquids, a calibration curve was drawn by plotting the retention times of 7 different pure n-paraffins ranging from C8 to c14 against their boiling points, by actually injecting a synthetic mixture of them on a special SED packed column, (developed at CFRI) maintained under experimental conditions exactly similar to those used for analyzing coal-hydogenate samples. The synthetic mixture of n-paraffin (BDH make) as well as th primary and upgraded coal-hydrogenate samples were injected (0.1 µl) into the gas chromatograph by means of a 10 µl Hamilton micro syringe. The instrument used for the present SG-DC analysis work was a Perkin-Elmer (USA, model 3920B). The experimental details and the GC conditions are given in TABLE 2.

The areas of the peaks on the GCD chromatograms were measured by using a planimeter. The calculations for the initial boiling point (IBP) and final boiling point (FBP), percent recovery etc. were made by following the procedure prescribed for ASTM2887 method[4].

A Baired and Tatlock apparatus was employed for performing the actual ASTM D286[1] single theoretical plate distillation of IBP-180°C of the primary coal-hydrogenate. Subsequently, GCD of the same sample was done following the guidelines and procedure of ASTM 2887[4] for the purpose of comparison.

RESULTS AND DISCUSSION

The calibration curve with n-paraffins plotted between boiling points and the retention time is shown in figure 1. The boiling range distribution curve of the primary coal-hydrogenate fraction (IBP-180°C), generated from its GCD chromatogram, and the actual ASTM D86 distillation curve of the same sample obtained from the distribution in Baired and Tatlock apparatus are de-
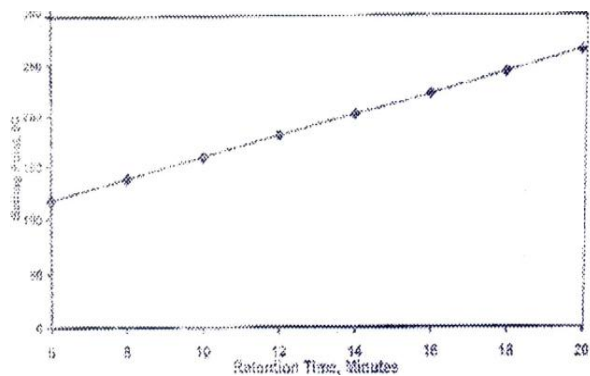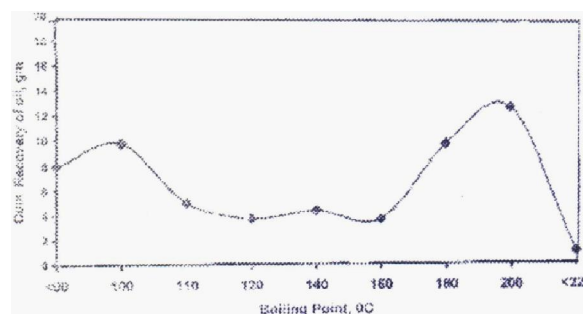
Figure 1 : Calibration curve with n-paraffins

Figure 2 : Distribution of different boiling range hydrocarbons in the primary coal-hydrogenate (IBP-180°C) determined by ASTM D-86 method and generated from SGCD chromatogram
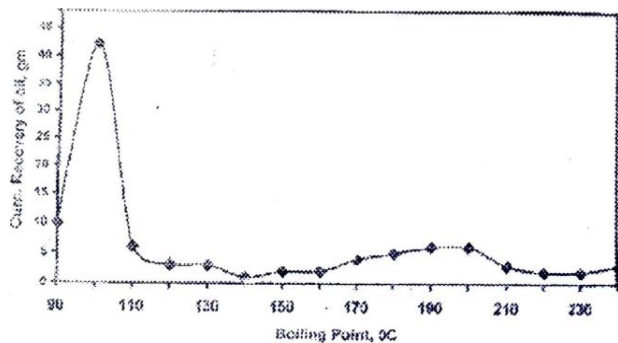

Figure 3 : Distribution of different boiling range hydrocarbons in the primary coal-hydrogenate (IBP-180°C) determined by actual ASTM D-86 method
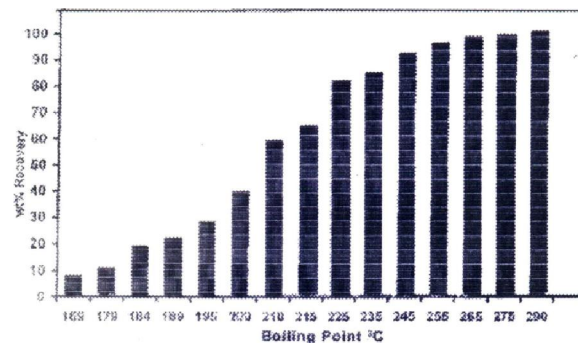

Figure 4 : Histogram showing distribution of different boiling range hydrocarbons in the upgraded coal-hydrogenate in presence of Ni-Mo catalyst
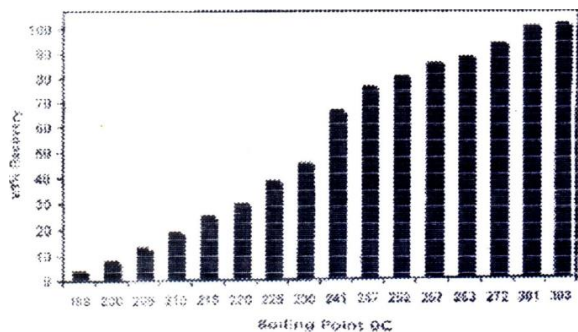

Figure 5 : Histogram showing distribution of different boiling range hydrocarbons in the upgraded coal-hydrogenate in presence of Ni-W catalyst
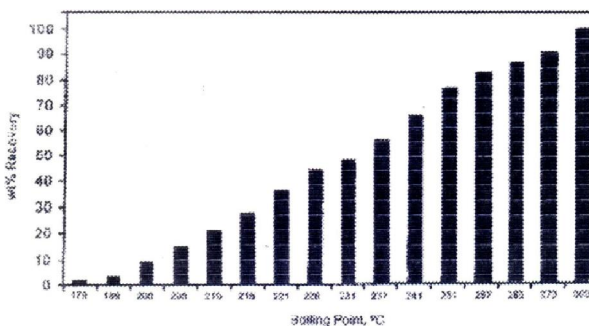

Figure 6 : Histogram showing distribution of different boiling range hydrocarbons in the upgraded coal-hydrogenate in presence of Co-Mo catalyst

picted in figure 2 and 3 respectively. The distribution of different boiling range hydrocarbons in the Raniganj Coal-hydrogenates determined by ASTM2887 (GCD) is shown in Table-III. .Further, the corresponding boiling range distribution patterns of the upgraded coal-hydrogenate samples obtained with three commercial catalysts, viz., Ni-Mo, Ni-W, and Co-Mo, all supported over alumina, are shown in TABLE 4 and also depicted as histograms in figure 4, 5, and 6 respectively.

It was observed that on the basis of the calibration cure (Figure 1), the conversion of retention times of coal-derived liquids into their corresponding boiling points was possible which helped in calculating the boiling range distribution.

It may be seen from the nature of the two curves that the boiling range distribution of the sample under consideration, derived through the above mentioned two different methods, show a good similarity, though a little shift in the IBP (4°C less in case of ASTM86 method) and IBP (4°C more in case of ASTM D86 method) of

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TABLE 1 : Priximate and ultimate analyses of raniganj coal

(1) Proximate Analysis (*Air dried basis*)	
Element	%
Ash	24.2
Moisture	3.1
Volatile Matter	29.9
Fixed Carbon	42.8
(2) Ultimate Analysis (*dmmf basis*)	
Element	%
Carbon (C)	57.7
Hydrohen (H)	3.81
Nitrogen (N)	1.58
Sulphur (S)	0.40
Oxygen (O) (by difference)	36.64
(3) Calorific Value (kcal/kg) (*dmmf basis*)	**7900**

TABLE 2 : Details of the GC set-up and experimental conditions

Column	:	2 meter, 1/8" o.d, ss
Stationary phase	:	10% SE 30 on Ch-P (80 – 100 mesh)
Column temperature	:	initial 44 ^{o}C, final 200 ^{o}C
Temperature programming rate	:	@ 8 ^{o}C/ min
Injector temperature	:	250 ^{o}C
Detector interface temperature	:	250 ^{o}C
Detector used	:	FID
Detector gas, and flow rate	:	Nitrogen, 30 ml/min
Sample size	:	0.1 μl
Analysis time	:	less than 50 minutes

the sample was noticed. A little more than 55% recovery has been observed within 98°C (b.p.) in case of ASTM D86 method. On the other hand, a 58% wt recovery has been found to be there within 93°C (b.p.) in case of GCD method. The actual distribution of different range hydrocarbons present in the sample determined by GCD is shown in TABLE 3.

Also, the corresponding boiling range distribution patterns of the upgraded coal-hydrogenate samples obtained with three commercial catalysts, viz., Ni-Mo, Ni-W, and Co-Mo, all over alumina support, are shown as histograms in figure 3, 4, and 5 respectively.

By the ASTM D86 method of distillation, the amount of actual IBP-180°C fraction recovered showed a 15% deviation for the corresponding figures obtained from ASTM D2887 (GCD) method. The recovery of fraction boiling between IBP-220°C (by ASTM D26 method) deviated from the corresponding value determined by GCD method by 12.7%. The reason for such deviation in the IBP-180°C may be attributed to the relative ease of azeotrope formation[5].

As during the upgrading reactions with the aforementioned three catalysts, reaction parameters like temperature, pressure, and duration were kept constant, the only change expected to be observed in the product patterns is obviously due to the effect of the catalysts itself. From the three boiling range distrinution graphs of the upgraded coal-hydrogenates obtained with Ni-Mo, Ni-W, and Co-Mo catalysts (Cf. Figure 3, 4,

and 5 respectively), it is apparently clear that all the three products are almost having a similar pattern under the set of reaction parameters used for upgrading. This may be due to the fact that the set reaction parameters that were chosen might not be the optimum for the best catalytic activity of the catalysts used. However, there is some original variation in their actual yields (wt %) corresponding to the boiling range distribution, as shown in TABLE 4.

From a comparison of data in TABLE 3 and 4, it is observed that pattern of distribution of boiling range of coal-hydrogenates changes altogether in that where the maximum recovery (96.5%) of coal hydrogenates is obtained in the boiling range IBP-180°C, the maximum recovery (in the range 74.5-82%) in the presence of catalysts shifts, in general, to the boiling range 180-250°C, being maximum for Ni-Mo catalyst, followed by 76.5% for Ni-W catalyst and 74.5% for Co-Mo catalyst. It is important to observe from Table-IV that in case of Ni-Mo catalyst, the recovery is distributed in the boiling ranges < 180°C and > 250°C too, being significant 12% in the former less (6.0%) in the latter. Contrary to this observation, the recovery in case of Ni-W catalyst is seen to have been restricted to the boiling ranges 180-250°C and > 250°C only, being a maximum of 76.5% in the former and 23.5% in the latter. Furthermore, the recovery of the coal-hydrogenates in case of Co-Mo catalyst is interestingly observed to have been distributed in all the three boiling ranges, i.e. IBP - 180°C, 180-250°C, and > 250°C, being maximum 74.5 % for the < 180°C fraction, followed by 24% for the > 250°C fraction and a minuscularly small (mere 1.5%) for the < 180°C cut. The variation

TABLE 4 : Boiling range distribution of upgraded coal-hydrogenates by SGCD (wt%)

Coal-htdrogenate different catalysts	Recovery (wt %) in the boiling range distribution		
	< 180°C	180-250°C	> 250°C
Ni-Mo	12.0	82.0	6.0
Ni-W	0.0	76.5	23.5
Co-Mo	1.5	74.5	24.0

TABLE 3 : Distribution of different boiling range hydrocarbons in the Raniganj Coal-hydrogenates determined by ASTM2887 (GCD)

	Boiling range distribution		
Fraction	IBP-180°C	180-224°C	Residue > -224°C
% wt recovery	96.5	1.8	1.7

in the % recovery of the coal hydrogenates and a shift in their boiling ranges might possibly be due to the activity, selectivity and specificity of the individual catalysts (Ni-Mo, Ni-W, and Co-Mo) used for the upgradation of coal hydrogenates.. Therefore, the distribution pattern of the coal-hydrogenates in different boiling ranges studied by SGCD method is also helpful in the selection of different catalysts for obtaining specific product yield.

To summarize, the technique of Simulated Gas Chromatographic Distillation (SGCD) has advantageously been used for studying the precise boiling range distribution characteristics of different fractions of both non-catalytic and catalytic bituminous Raniganj coal hydrogenation (coal-hydogenates). While the maximum yield (96.5%) for the non-catalytic hydrogenation is obtained in the boiling range IBP-180°C, the. maximum yield (74.5-82.0 wt%) in case of catalytically upgraded hydrogenates gets shifted to in the higher boiling range, i.e. 180 -250°C.

CONCLUSIONS

The important conclusions drawn from the experimental results of this study are encapsulated below:

(1) Simulated Gas Chromatographic Distillation (SGCD) is a useful, rapid, efficient, accurate, and superior analytical technique for studying the precise boiling range distribution characteristics of different fractions of non-catalytic and catalytically upgraded coal-hydogenates.

(2) The maximum recovery of the coal hydrogenates, obtained after hydrogenation of bituminous Raniganj coal without any catalyst, is 96.5 wt%, which is in the boilimg range lBP-180°C ; the recovery in the boiling ranges 180-224°C and Residue > -224°C is very small, being 1.8 and 1.7 wt% respectively.

(3) However, the recovery of coal hydrogenates in the presence of different catalysts, in general, is maximum in the boiling range 180-250°C, being 82.0, 76.5 and 74.5 wt% with Ni-Mo, Ni-W, and C0-Mo catalysts respectively.

(4) The analytical data obtained from the SGCD method is useful in the selection of catalyst for the liquefaction of coals and their subsequent upgradation effectively. The GCD analytical data is also useful for the product yield calculations, material balance,and also for understanding the correlation between the physical properties of the products in different boiling range of the coal-derived hydrogenates.

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