

A Reactive Analytical Approach for the Estimation of Olefinic Content in Gasoline-Range Hydrocarbons by Gas Chromatography

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Abstract

The estimation of olefinic content in conversion processes such as the etherification of olefins in fluid catalytic cracking (FCC) gasoline is essentially required. Gas chromatography (GC) is the well-established method for the quantitative analysis of olefins in etherification processes. The current state-of-the-art GC methods employing highly specific long single capillary columns such as Petrocol-DH are being used for the analysis of gasoline-range hydrocarbons. However, the method needs many standard reference samples of respective components in a complex mixture of hydrocarbons, which limits the scope of the analytical method. The alternative approach followed by this investigation is based on the reactive method of the analysis of olefins in FCC light gasoline by subjecting them to hydrogenation and estimating the olefinic content by GC comparing the gas chromatograms of the original feed and hydrogenated product using a Petrocol-DH column. A decrease in the quantity and disappearances of the peaks are assumed as olefins, and their number and total composition is calculated. In this study the bromine number method is used to estimate the olefinic content for a comparison of results with the adopted proposed methodology. The adopted methodology quantitates olefinic content in FCC light gasoline, which is comparable with reported literature values and the bromine number method. With the availability of standard reference samples of some important major reactive olefins, the adopted methodology can also give component-wise analysis as well as total olefinic content in a single step in processes such as etherification. The methodology can be also useful in reactions in which the conversion of total olefinic content is needed such as hydration, esterification, and alkylation of olefins in a complex mixture of hydrocarbons apart from the etherification of olefins in FCC gasoline.

Introduction

The estimation of olefinic content in processes such as the etherification of olefins in light fluid catalytic cracking (FCC)

gasoline is essentially required to determine the conversion of olefins to environment-friendly products (1,2). FCC light gasoline is a major contributor of olefins in gasoline stream. Because of the negative impact of olefins on the environment, their conversion shifted to the etherification processes because of the clean-burning fuel characteristics of product ethers. Gas chromatography (GC) is the well-established method for the quantitative analysis of olefins in gasoline-range hydrocarbons (3–11) and olefinic conversions during etherification processes (12–20). The current state-of-the-art GC methods employing highly specific single capillary columns, such as the Petrocol-DH (Supelco, Bellefonte, PA) with different lengths, are being used for the quantitative analysis of gasoline-range hydrocarbons. However, the method needs many standard reference samples of respective components in a complex mixture of hydrocarbons, which limits the scope of the analytical method.

The alternative approach followed in this investigation is based on the reactive method of analysis. FCC light gasoline is hydrogenated in the presence of a commercial catalyst under the optimum reaction conditions in order to ensure the complete saturation of olefins. This study describes the alternative method of the analysis of olefins in FCC light gasoline by subjecting them to hydrogenation and estimating the olefinic content by GC comparing the gas chromatograms of the original feed and hydrogenated product using a Petrocol-DH column. With the availability of standard reference samples of some important major reactive olefins, the adopted methodology can also give component-wise analysis as well as total olefinic content in a single step by GC analysis. The required experimental facilities described in this work are commonly available and essentially used in processes such as etherification. Therefore, the adopted methodology can be used as a routine analytical procedure for the estimation of olefinic content in these processes.

For general purposes, the bromine number method is used for the estimation of olefinic content in petroleum distillates and products, which is cumbersome, time-consuming, and requires a number of hazardous chemicals. In this study the

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bromine number method has been used to estimate the olefinic content for a comparison of results with the adopted proposed methodology (21).

We were tempted to adopt this methodology while carrying out the etherification reactions because it was tough to identify all of the olefin isomers in the C₆ and C₇ hydrocarbons. Therefore, the idea was that apart from conversion changes in important major identified olefins, it could be possible to give the conversion of the total olefinic content by GC.

Light FCC gasoline (30–60°C and 30–105°C) was selected for detailed analysis to identify the components and quantitate the olefinic content by the proposed methodology. The reactive analytical approach adopted in this investigation is not available in the published literature to the best of our knowledge. Several other analytical methods such as fluorescent indicator adsorption (FIA) (22), high-performance liquid chromatography (23–26), supercritical fluid chromatography (27–30), mass spectrometry (31), and infrared (32,33) and ¹H/¹³C nuclear magnetic resonance (34,35) spectroscopy have been employed to determine hydrocarbon types present in

naphtha and gasoline-range hydrocarbons. The detailed overview of these analytical methods for the estimation of olefins in a complex mixture of hydrocarbons is beyond the scope of this study.

Experimental

The series of experiments were conducted in a continuous tubular reactor in order to carry out hydrogenation reaction. The optimum reaction conditions used were: a temperature of 90°C, a pressure of 7.0 kg/cm² (H₂) with a continuous flow of hydrogen gas, and an LHSV 7 h⁻¹ of feed FCC gasoline cut 30–105°C. The catalyst used was commercial E85510B/D 5%, Pd aminopolysiloxane microsphere (5.0 g, Degussa AG, Frankfurt am Maine, Germany). The total time for experimentation was 4 h (2 h for stabilization and 2 h for sample collection). The hydrogenation reaction was also performed in an autoclave under similar experimental conditions of temperature and pressure as mentioned previously with 200 mL

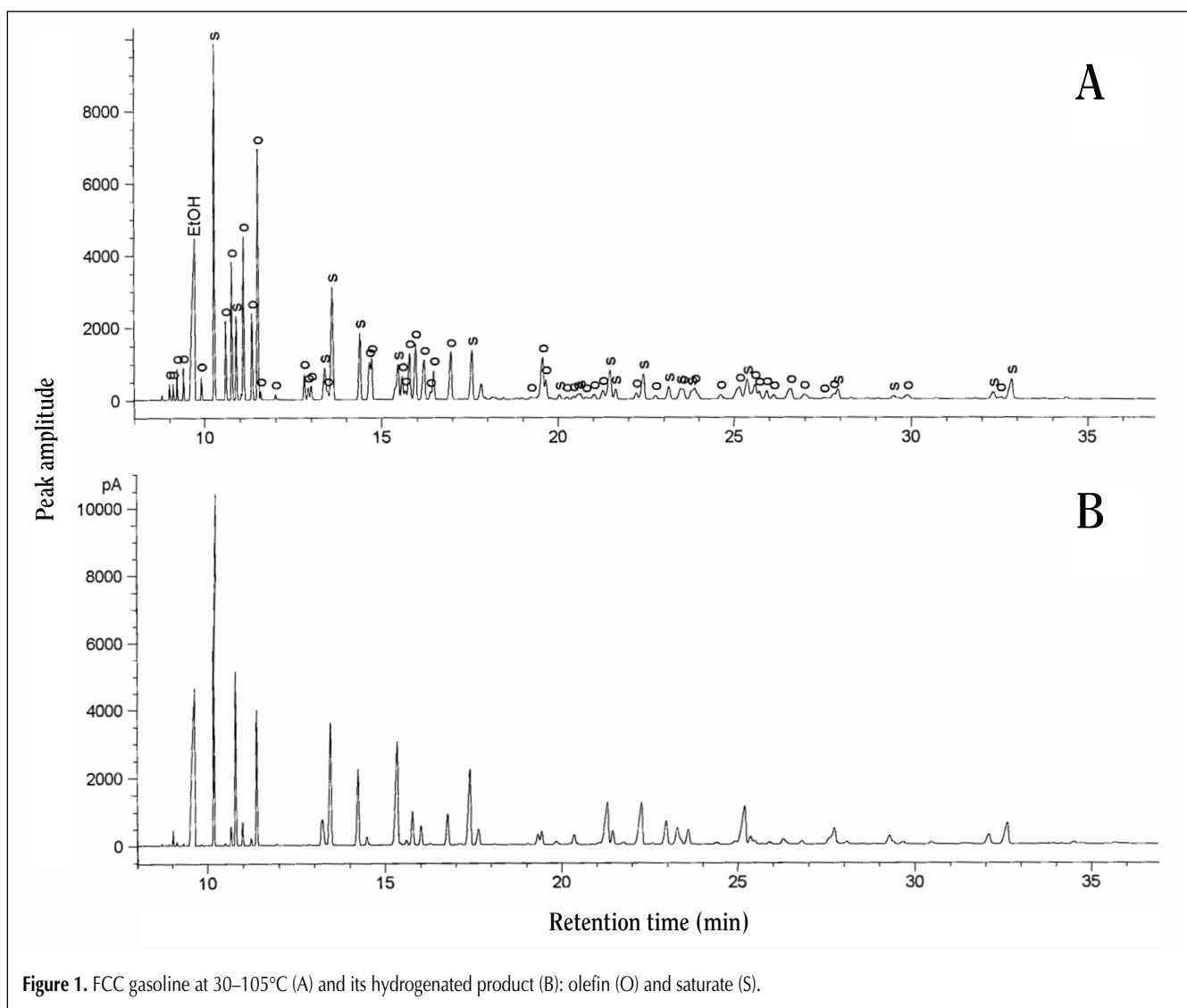


Figure 1. FCC gasoline at 30–105°C (A) and its hydrogenated product (B): olefin (O) and saturate (S).

FCC gasoline (30–105°C) without a continuous flow of H₂ gas. In addition, a hydrogenation experiment was also performed in an autoclave with 200 mL FCC gasoline (30–60°C) at 100°C, 10 kg/cm² H₂ gas, and a reaction time of 3.0 h with the same catalyst (10.0 g). The source of these two FCC gasoline cuts was the same.

A Hewlett Packard (Wilmington, DE) 6890 GC system with a flame ionization detector (FID) was interfaced with the computer. Analytical data were generated using a Supelco Petrocol DH capillary column (100-m × 0.25-mm i.d., 0.5 μm) connected to an FID, and analysis was carried out using HP ChemStation software. The analytical conditions were followed for getting the clear-cut separation of all the components present in these boiling ranges. The chromatograms were generated using GC-grade highly ultrapure nitrogen (1.9 mL/min con-

stant flow, 26.0 cm/s average velocity) as the carrier gas with a split ratio of 50:1. The rise in oven temperature was programmed to get the clear separation of individual components in the hydrocarbon mixtures.

The FID was set at a temperature of 240°C and used H₂ (30 mL/min) fuel, oxidant air (300 mL/min), and diluted N₂ (28.1 mL/min).

The injector's temperature was 210°C, and the temperature program was as follows: the first temperature, time, and rate were 38°C, 15 min, and 1°C/min, respectively; the second temperature, time, and rate were 60°C, 20 min, and 2°C/min, respectively; and the third temperature and time were 200°C and 0.0 min, respectively. The total time was 127 min. The sample size was syringe injection individuals of 1.0 μL + 1.0 μL airplug.

Table I. Components Identified by Reference Samples and Adopted Procedure in FCC Gasoline Ranging from 30–60°C and 30–105°C

wt%	Retention time (min)	Identified by reference sample	Identified by hydrogenation	wt%	Retention time (min)	Identified by reference sample	Identified by hydrogenation
0.32	8.999	unidentified	olefin	0.22	22.759	unidentified	olefin
0.28	9.104	unidentified	olefin	0.51	23.539	unidentified	olefin
0.53	9.213	unidentified	olefin	0.98	23.870	heptene	olefin
0.56	9.396	unidentified	olefin	0.35	24.607	unidentified	olefin
9.84	9.721	ethanol		1.42	25.139	<i>trans</i> -3-heptene	olefin
0.49	9.904	3-me*-1-butene	olefin	1.26	25.579	<i>cis</i> -3-heptene	olefin
1.81	10.591	pentene-1	olefin	0.45	25.696	unidentified	olefin
3.52	10.761	2-me-1-butene	olefin	0.54	25.911	<i>trans</i> -2-heptene	olefin
4.05	11.095	<i>trans</i> -2-pentene	olefin	0.30	26.111	unidentified	olefin
2.27	11.335	<i>cis</i> -2-pentene	olefin	1.13	26.590	unidentified	olefin
6.74	11.502	2-me-2-butene	olefin	0.52	26.968	<i>cis</i> -2-heptene	olefin
0.15	11.571	<i>trans</i> -1,3-pentadiene	olefin	0.14	27.526	unidentified	olefin
0.14	11.990	3-me-1,2-butadiene	olefin	0.34	27.801	unidentified	olefin
0.79	12.806	4-me-cyclopentene	olefin	0.45	29.883	unidentified	olefin
0.39	12.914	4-me-pentene-1	olefin	0.18	32.508	unidentified	olefin
0.47	12.995	3-me-pentene-1	olefin	7.95	10.267	isopentane	saturate
0.24	13.457	2,3-di-me-butene-2	olefin	1.90	10.890	pentane	saturate
1.61	14.646	2-me-pentene-1	olefin	1.78	13.382	2,3-di-me-butane	saturate
1.40	14.706	1-hexene	olefin	5.34	13.597	2-me-pentane	saturate
1.04	15.568	unidentified	olefin	2.77	14.377	3-me-pentane	saturate
0.37	15.656	unidentified	olefin	2.18	15.453	<i>n</i> -hexane	saturate
2.18	15.779	<i>trans</i> -2-hexene	olefin	2.49	17.546	me-cyclopentane	saturate
2.46	15.950	2-me-pentene-2	olefin	0.27	20.029	3,3-di-me-pentane	saturate
2.13	16.191	3-me-pentene-2	olefin	0.23	20.545	unidentified	saturate
0.29	16.372	unidentified	olefin	0.31	20.617	cyclohexane	saturate
1.25	16.460	<i>cis</i> -2-hexene	olefin	2.13	21.464	2-me-hexane	saturate
2.34	16.949	3-me- <i>trans</i> -2-pentene	olefin	0.54	21.626	2,3-di-me-pentane	saturate
0.16	19.226	unidentified	olefin	1.64	22.412	3-me-hexane	saturate
2.76	19.551	unidentified	olefin	0.80	23.137	<i>cis</i> -1,3-dimethylpentane	saturate
0.91	19.645	unidentified	olefin	0.74	23.472	3-ethyl-pentane	saturate
0.12	20.241	unidentified	olefin	0.51	23.791	unidentified	saturate
0.16	20.424	unidentified	olefin	1.67	25.358	<i>n</i> -heptane	saturate
0.16	20.775	unidentified	olefin	0.73	27.917	me-cyclohexane	saturate
0.36	21.013	unidentified	olefin	0.35	29.484	ethyl-cyclopentane	saturate
0.61	21.263	unidentified	olefin	0.65	32.300	unidentified	saturate
0.39	22.209	unidentified	olefin	1.73	32.824	unidentified	saturate

* me, methyl.

Results and Discussion

The results from the gas chromatograms included C₅-, C₆-, and C₇-range hydrocarbons in the 30–105°C cut FCC gasoline and C₅- and C₆-range hydrocarbons in the 30–60°C cut FCC gasoline with a very small fraction of C₄ in both the cuts. FCC light gasoline contains olefins in the C₅, C₆, and C₇ range with a number of isomers. As a result of hydrogenation these olefins are converted to their corresponding saturates. The gas chromatograms of the hydrogenated product were compared with the original feed. Either a decrease in quantity or disappearances of the peaks were assumed as olefins and their number and total composition were calculated.

The light cut naphtha (LCN) is approximately 50% of the whole FCC gasoline cut and accounts for 15–20% of the total gasoline pool. The composition of the total olefins is 40–65% in LCN in the boiling range of 35–100°C (2,36). In this case the FCC gasoline boiling range (30–105°C) contained a 52–54 mass percentage of olefinic content as determined by the bromine number method (21).

The GC analysis showed that FCC gasoline (30–105°C) con-

tained 74 components having a minimum quantity of 0.12 wt%. Quantitation was done using an FID assuming that the response factors were the same for all the individual hydrocarbons. The generated gas chromatograms can be seen in Figures 1A and 1B for reactants and hydrogenated products, respectively, in a tubular reactor showing that there are 45–50 components either completely disappearing or decreasing in quantity from 10% to more than 70–80% with a simultaneous increase in the quantity of 18–20 components. The hydrogenated product contained 47 components only, which shows that 27 components have completely disappeared. The results clearly indicated that the components that were disappearing or decreasing in quantity hydrogenated during the reaction. The simultaneous increase in the quantity of other components showed that these were saturates that were increasing because of the hydrogenation of corresponding olefins. The components that were disappearing or decreasing in quantity are denoted by 'O' (olefin), and the components that were increasing in quantity are denoted by 'S' (saturate). In order to confirm these findings, the two categories of hydrocarbons (i.e., olefins and saturates) were further identified by available

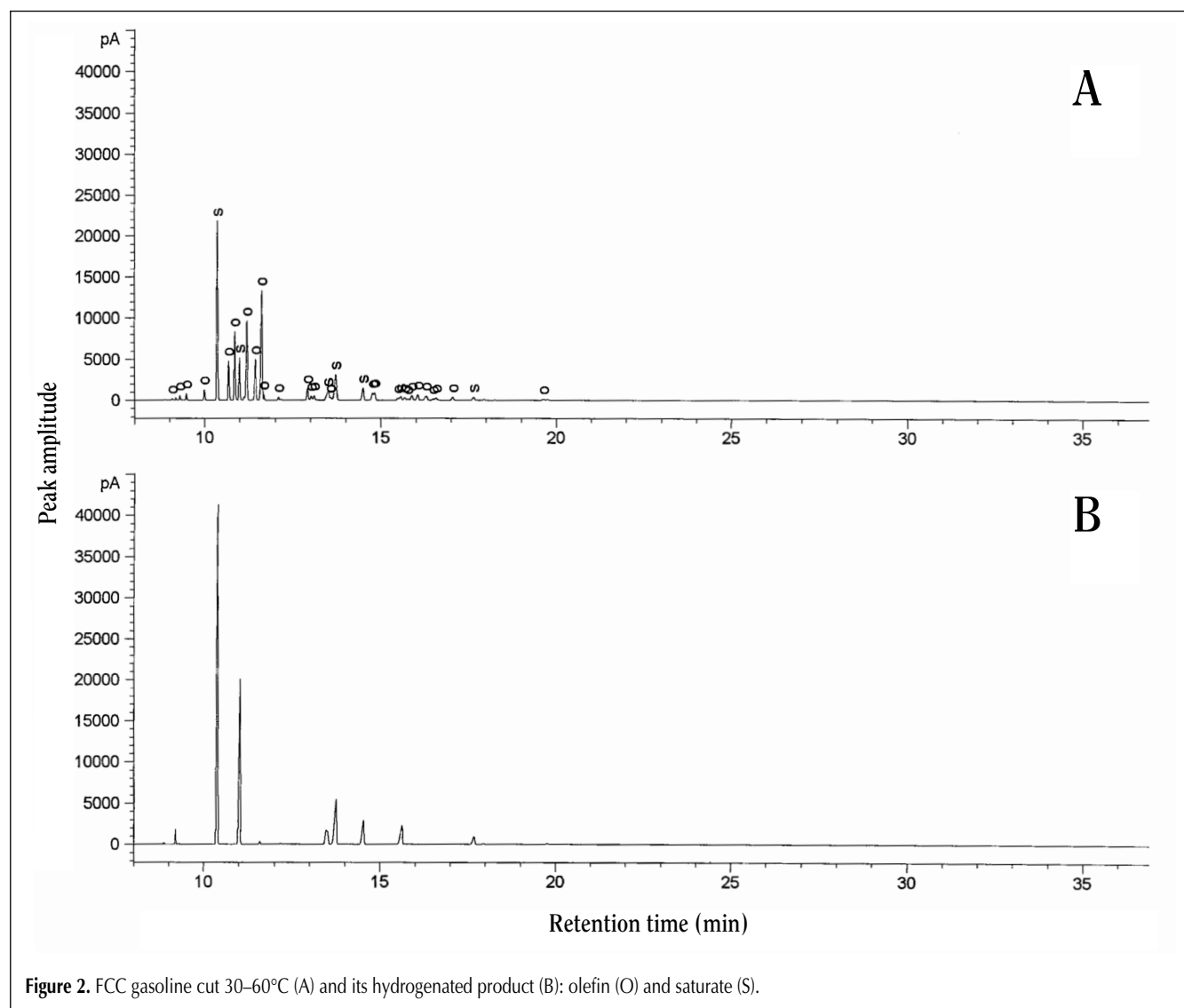


Figure 2. FCC gasoline cut 30–60°C (A) and its hydrogenated product (B): olefin (O) and saturate (S).

PIANO standard reference samples (Supelco). Approximately 50 components were identified in FCC gasoline (30–105°C). These identified components were olefins, paraffins, isoparaffins, and naphthenes. The identified olefins and saturates by reference samples were also categorized as 'O' and 'S' by the adopted hydrogenation methodology. The details of these results are shown in Table I.

The comparison of gas chromatograms of the original feed and hydrogenated product in an autoclave indicated a similar pattern. However, because of more severe reaction conditions, the hydrogenation in the autoclave with FCC gasoline (30–60°C) appeared complete. FCC gasoline (30–60°C) contained 36 components, and the hydrogenated product contained only 12 components. The generated gas chromatograms that can be seen in Figures 2A and 2B for the reactants and hydrogenated products in the autoclave reactor showed a complete disappearance of 24 components and a decrease in the quantity of 3 components in the hydrogenated product of FCC gasoline (30–60°C) with a simultaneous increase in the quantity of other remaining components. The result after all of the previous experiments showed that the total olefinic content estimated by the methodology of this investigation gave approximately 57.0–58.0 wt% of olefins in FCC gasoline (30–105°C) (total olefinic content = 57.0–58.0 wt%, after excluding ethanol weight percentage and then calculating on the basis of 100 wt% for FCC gasoline), and in the hydrogenated product of FCC gasoline (30–105°C) there was approximately 19–20 wt% of olefins with a 66.0% overall conversion of olefins. Therefore, the olefinic content estimated by the methodology of this investigation was closely comparable with literature values (2,36) as well as the value obtained by us determined by the bromine number method.

Conclusion

This is a primitive work in this direction with an indication of getting significant results that can be very useful in reactions in which the conversion of total olefinic content is needed such as the etherification of olefins in FCC gasoline, hydration, esterification, and alkylation of olefins in a complex mixture of hydrocarbons. Thus, the reactive analytical methodology developed in this investigation can give total olefinic content in a gasoline-range complex mixture of hydrocarbons by GC analysis. With the availability of standard reference samples of some important major reactive olefins, the adopted methodology can also give component-wise analysis as well as total olefinic content in a single step in processes such as etherification.

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