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Effect of aromatic additives on the physiochemical properties of petroleum distillates

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Abstract

The potential of four aromatic additives namely benzene, toluene, xylene, phenol and admixture of the four known as BTXP mixture on the physico-chemical enhancement properties of premium motor spirit (PMS), dual purpose kero (DPK) and automotive gas oil (AGO) has been investigated in this work at varying ratios. Additives to distillate volume ratios of 10:90, 20:80,30:70 and 40:60 were used. The results show that as the volumes of additives in the 100ml mixture increase the densities, flash points, boiling points and viscosities of the distillates increase. Also as the volumes of additives in the 100ml mixture increase, the degree API, thermal conductivities, specific heat capacities and heat capacities decrease. It is note worthy that the degree of influence is dependent on the different levels of additives added. The best additive to volume ratio of 10:90 was obtained for all the fractions. Xylene was adjudged as the best additive that can be used to obtain the best quality distillates.

1. Introduction

Crude oil has no inherent value without refining to process it into usable fractions, which have greater intrinsic value than the crude oil itself. Most of these fractions obtained from refining such as premium motor spirit, dual purpose kero, automotive gas oil and other heavier distillates require additives in order to perform optimally. Lubricating oil also requires additives to give the base oil desirable characteristics which they lack (Oyekunle and Ochem, 2000). The use of additives in petroleum processing is to enhance the physico-chemical properties of petroleum distillates. Additives are categorized according to the physical properties they modify. Some of the additives are used to enhance the physical properties. While others are used to modify the chemical properties. Properties that are enhanced by additives include flash point, degree API, density, boiling point, specific heat capacity, heat capacity, thermal conductivity, viscosity and octane rating.

An additive is a chemical substance, usually added to a product to improve existing characteristics. Aromatic additives are cyclic hydrocarbons with benzene as their parent compound. They posses high density and sweet smelling odour as distinguishing property. The commonly used additives for improving octane rating of premium motor spirit are triethyl lead and tetraethyl lead (Nelson, 1958).

As a result of the adverse environmental impact of these additives, the need to develop other additives, which are environmentally friendly, becomes apt.

In this paper, the use of benzene, toluene, xylene, phenol and admixture of BTXP as alternative in place of convectional additives like triethyl lead for enhancing the physico-chemical properties of petroleum distillates is explored with a view to determining the best of the five options and optimal formulation.

2. Materials and Methods

2.1. Materials

The aromatic additives used were sourced locally. The petroleum fractions PMS, DPK and AGO from PPMC of NNPC Enugu depot. The benzene, toluene, xylene and phenol were of analar grade. The distillate fractions used have no commercial additives. The instrument used include testa still, the thermometer and hydrometer.

2.2. Methods

2.2.1. Distillation test (boiling point)

10ml of benzene was mixed with 90ml kerosene into a bottom flask. The mixture was agitated to ensure proper mixing and subsequently poured into a steel-heating cup and inserted into the testa still for heating. The heating was monitored via the inbuilt thermometer of the testa still and the boiling was recorded. The experiment was repeated using 20ml:80ml, 30ml: 70ml, and 40ml: 60ml of benzene/kerosene mixtures and for the other four additives in the same volume ratios as for benzene and kerosene.The above experiments were also carried out for automotive gas oil (AGO) and premium motor spirit (PMS) and the results recorded.

2.2.2. Flash point test

A mixture of 10ml of benzene and 90ml of kerosene was measured into the heating bowel and placed into a heating bath containing water. A thermometer was fixed on its stand. Depressing the button ensured heat supply and subsequently the gas nozzle was opened and heat was supplied. As the heating continued, the vapour taper was opened intermittently to supply the vapour of kerosene directly to the flame. The temperature at which the vapour ignites temporarily was measured. The same experiment was repeated for 20ml: 80ml, 30ml: 70ml and 40ml: 60ml of benzene/kerosene mixture and for the other four additives. The values were recorded. For automotive gas oil (AGO), the mixtures were prepared as above but with diesel as the fraction. The mixture was poured into the steel heating cup and heat was supplied directly via the heating element. As the heating continued, the mixture was automatically stirred. The taper was intermittently opened and the temperature at which it ignites was recorded. Premium motor spirit was not tested for flash point for some because it is very explosive even below ambient condition.

2.2.3. Density test

A mixture of 10ml, 90ml, 20ml: 80ml, 30ml: 70ml, 40ml: 60ml, of each additive to each fraction was prepared in the flasks. Each mixture was tested with the appropriate hydrometer bottle. The results were recorded. Viscosity, degree API, specific heat capacity, thermal conductivity and heat capacity were calculated using empirical formulae.

(1) Viscosity:- $\mu_b = O.O\ 1\rho_b^{\ 0.5}$ (Coulson and Richardson 1993)

(2) Thermal conductivity:- $K = 3.56 \times 10^{--5}\ Cp\ (\rho^4/m)^{1/3}$ where m = molecular weight. (Coulson and Richardson 1993)

(3) Heat capacity = Summation of individual heat capacities of the elements of the compound. (Kopp's Law) (Coulson and Richardson 1993)

(4) Specific heat capacity = Heat capacity/molecular weight. (Coulson and Richardson 1993)

(5) Degree API = $\frac{141.5}{131.5}$

Specific gravity $60/60^0$F

3. Results and Discussion

Table 1
Standard Values of the fractions used

Component properties	Dual purpose Kero	Automotive gas oil	Premium motor spirit
Boiling point(^oC)	238—288	340—360	175—210
Flash point	42—48	60—110	Ambient
Density (Kg/m^3)	800—830	830—870	700—770
API	39-41	30—33	59—62
Viscosity (mNs/m^2)	0.2828—0.2881	0.2881—0.2950	0.2645—0.2775
Thermal conductivity w/m ^oC	2.178—2.260	2.260—2.356	1.954—2.150
Heat Capacity J/Mol ^oC	0.2840—0.2911	0.2930—0.3036	0.2550—0.2803

Source: NNPC

3.1. Density

Table 2
Effect of aromatic additives on densities of the fractions

		PMS	DPK	AGO
Benzene ml	Fractions ml	Density kg/m^3	Density kg/m^3	Density kg/m^3
10	90	743.50	825.38	861.86
20	80	755.38	830.80	863.73
30	70	767.64	837.00	865.80
40	60	780.30	842.67	867.50
Toluene ml	Fractions ml			
10	90	743.65	824.70	860.60
20	80	755.67	828.77	861.19
30	70	768.10	833.67	861.79
40	60	780.94	837.74	862.39
Xylene ml	Fractions ml			
10	90	743.65	824.70	860.79
20	80	755.67	829.46	861.59
30	70	768.10	833.57	862.38
40	60	780.94	838.22	863.18
Phenol ml	Fractions ml			
10	90	706.73	839.94	877.82
20	80	782.32	861.60	896.39
30	70	810.16	883.39	915.76
40	60	840.06	906.86	935.99
BTXP ml	Fractions ml			
10	90	743.80	824.70	860.99
20	80	755.98	829.46	861.98
30	70	768.86	839.27	862.98
40	60	781.06	840.54	863.97

The density of premium motor spirit is generally less than that of automotive gas oil dual purpose kero. As the volume of additives in 100ml of the mixture increases, the densities of the mixtures increase progressively. Ratios of 10:90, 20:80 and 30:70 for benzene, toluene, xylene and BTXP volume ratios showed values within the standard values. The exception was of phenol additive which only the 10:90 volume ratio complied with the standard . The result in Table 2 also showed that 40:60 volume ratio is not a good blend in all the additives used.

It was observed that the density for DPK increases as the volume additives in 100ml of the mixture increases. The ratio of 10:90 and 20:80 for benzene, toluene, xylene and BTXP showed values that are in the standard range. The blend in the phenol additives did not conform at all to the standard. All the additives to fractions volume ratios in AGO gas oil showed standard compliance as regards densities with the exception of phenol. The densities obtained for phenol deviated completely from the standard range as shown in Tables 1 and 2.

3.2. Flash Point

Table 3.
Effect of aromatic additives on flash points of the fractions

		PMS	DPK	AGO
Benzene ml	Fractions ml	Flash Point ^oC	Flash Point ^oC	Flash Point ^oC
10	90	Ambient temp	44.00	64.60
20	80	“	45.40	65.80
30	70	“	46.30	67.00
40	60	28.00	47.30	69.00
Toluene ml	Fractions ml			
10	90	Ambient temp.	43.80	64.00
20	80	“	44.40	65.80
30	70	“	45.60	67.00

40	60	28.00	46,00	69.00
Xylene ml	Fractions ml			
10	90	Ambient temp.	43.70	63.30
20	80	"	44.80	65.00
30	70	"	45.40	66.00
40	60	28.00	46.70	68.00
Phenol ml	Fractions ml			
10	90	Ambient temp.	44.00	65.00
20	80	29.00	46.00	68.00
30	70	36.00	49.00	70.00
40	60	28.00	55.00	74.00
BTX P ml	Fractions			
10	90	Ambient temp.	43.60	64.00
20	80	"	43.80	66.00
30	70	"	45.50	68.00
40	60	28.00	46.00	70.00

The ratios of 10:90, 20:80 and 30:70 for benzene, xylene and BTXP indicated values of flash points in conformity with the standard values. The result in Table 3 showed that only 10:90 volume ratio is the only ratio that conformed with the standard as regards to phenol. The flash points for all the additives to fractions volume ratios conformed to the standard values for DPK. Only 10:90 and 20:80 volume ratios of phenol met the standard values. For the AGO all the additives to fractions volume ratios conformed to the standard range as depicted in Tables 1 and 3. From the whole results it can be deduced that the flash points increase as the volume additives in 100ml of mixture increase as shown in Table 3

3.3. Boiling point

Table 4
Effect of aromatic additives on boiling points of the fractions

		PMS	DPK	AGO
Benzene ml	Fractions ml	Boiling Point °C	Boiling Point °C	Boiling Point °C
10	90	206.00	241.80	345.00
20	80	209.00	243.00	346.50
30	70	211.00	246.00	348.00
40	60	214.00	251.00	350.
Toluene ml	Fractions ml			
10	90	205.00	240.00	344.80
20	80	208.00	243.00	345.70
30	70	212.00	246.00	346.00
40	60	215.00	249.00	348.00
Xylene ml	Fractions ml			
10	90	205.00	240.;00	345.00
20	80	208.00	242.00	346.00
30	70	212.00	245.00	347.00
40	60	215.00	249.00	347.80
Phenol ml	Fractions ml			
10	90	208.00	241.00	345.00
20	80	213.00	245.00	348.00
30	70	216.00	248.00	358.00
40	60	224.00	253.00	365.00
BTX P ml	Fractions ml			
10	90	207.00	240.00	345.00
20	80	210.00	243.00	347.00
30	70	213.00	245.00	347.80
40	60	218.00	248.00	350.00

The ratios of 10:90 and 20:80 in all the additives in premium motor spirit showed a reasonable compliance to the standard values as shown in Tables I and 4. But an exception was phenol additives in which only 10:90 volume ratio conformed to the standard. All the values for additives to fractions volume ratios fall within the range as depicted in tables 1 and 4 for DPK. For the automotive gas oil, all ratios complied with standard range with the exception of 40:60 volume ratios of phenol additives. The inference is that as the volume additives in 100ml of the mixture increase, the boiling points of the samples increase as shown in Table 4.

3.4. Viscosity

Table 5
Effect of aromatic additives on viscosity of the fractions

		PMS	DPK	AGO
Benzene ml	Fractions ml	Viscosity mNs/m^2	Viscosity mNs/m^2	Viscosity mNs/m^2
10	90	0.2728	0.2870	0.2936
20	80	0.2752	0.2880	0.2939
30	70	0.2776	0.2890	0.2942
40	60	0.2801	0.2900	0.2945
Toluene ml	Fractions ml			
10	90	0.2727	0.2870	0.2934
20	80	0.2748	0.2882	0.2935
30	70	0.2778	0.2892	0.2936
40	60	0.2793	0.2894	0.2937
Xylene ml	Fractions ml			
10	90	0.2727	0.2872	0.2934
20	80	0.2749	0.2880	0.2935
30	70	0.2771	0.2887	0.2947
40	60	0.2795	0.2895	0.2938
Phenol ml	Fractions ml			
10	90	0.2659	0.2898	0.2963
20	80	0.2797	0.2935	0.2990
30	70	0.2846	0.2972	0.3026
40	60	0.2899	0.3011	0.3059
BTX P ml	Fractions ml			
10	90	0.2727	0.2872	0.2934
20	80	0.2749	0.2880	0.2936
30	70	0.2773	0.2888	0.2948
40	60	0.2796	0.2899	0.2939

From Tables 5 and 1 it can be observed that for premium motor spirit 10: 90 and 20:80 volume ratios showed compliance with the standard in benzene and toluene while 10:90, 20:80 and 30:70 showed results within the standard range for xylene and BTXP mixture. For Phenol additive, only 10:90 volume ratio conformed to the standard.

For dual purpose kero, 10:90 and 20:80 volume ratios showed compliance for xylene, benzene and BTXP mixture. Toluene additive has 10:90 ratio as conforming to the standard while for phenol additive non of the ratios conformed.

All the additives to fractions volume ratios conformed to standard range in AGO as regards viscosity with the exception of phenol additives where non of the ratios conformed.

As the additives addition increase, the viscosity increases progressively in all the fractions. This is as a result of increase in the ring compound.

3.5. Degrees Api

Table 6
Effect of aromatic additives on api of the fractions

		PMS	DPK	AGO
Benzene ml	Fractions ml	^{O}API	^{O}API	^{O}API
10	90	58.00	40.00	32.60
20	80	54.30	38.60	32.30
30	70	52.00	37.40	31.90
40	60	47.50	36.20	31.50
Toluene ml	Fractions ml			
10	90	58.40	40.00	32.80
20	80	54.90	39.10	32.80
30	70	51.70	38.20	32.70
40	60	48.50	37.20	32.50
Xylene ml	Fractions ml			
10	90	58.40	40.00	32.80
20	80	54.90	38.70	32.60
30	70	51.60	38.30	32.66
40	60	48.50	37.30	32.40
Phenol ml	Fractions ml			
10	90	54.20	36.80	29.90
20	80	47.40	32.60	26.90
30	70	41.00	29.00	24.00
40	60	35.00	25.20	21.20
BTX ml	Fractions ml			
10	90	58.40	43.60	32.80
20	80	54.70	39.00	32.60
30	70	51.50	38.00	32.50
40	60	48.50	37.00	32.30

The degrees API of premium motor spirit for all the additives did not fall within the range of the standard values but as the volume of additives in 100ml mixture increases the degrees API decrease as shown in Tables 6 and 1. Similarly, as the volume additives in 100ml mixture increase, the degree API decreases in dual purpose kero. The values for phenol additives deviated from the standard for all the additive to fraction volume ratios. The 10:90 volume ratios for benzene and xylene conformed to the standard while 10:90 and 20:80 volume ratios of toluene and BTX P mixture also maintained standard values. The degree API for automotive gas oil maintained the trend as the other two fractions. The degree API decreases as the volume of additives in 100ml mixture increases indicating an increase in the density of the mixture. All the values of degree API for all the volume ratios of all the additives with the exception of phenol fall within the standard values as shown in Tables 6 and 1.

3.6. Heat capacities

Table 7
Effect of aromatic additives on the heat capacities of the fractions

		PMS	DPK	AGO
Benzene ml	Fractions ml	J/Mol ^{o}C	J/Mol ^{o}C	J/Mol ^{o}C
10	90	0.2644	0.2820	0.2935
20	80	0.2545	0.2739	0.2833
30	70	0.2477	0.2650	0.2732
40	60	0.2415	0.2560	0.2627
Toluene ml	Fractions ml			
10	90	0.2628	0.2837	0.2945
20	80	0.2570	0.2760	0.2854
30	70	0.2521	0.2684	0.2763
40	60	0.2470	0.2605	0.2672

Xylene ml	Fractions ml			
10	90	0.2628	0.2848	0.2957
20	80	0.2670	0.2784	0.2877
30	70	0.2550	0.2717	0.2798
40	60	0.2511	0.2650	0.2719
Phenol ml	Fractions ml			
10	90	0.2681	0.2865	0.2978
20	80	0.2619	0.2819	0.2918
30	70	0.2586	0.2812	0.2843
40	60	0.2560	0.2715	0.2791
BTXP ml	Fractions ml			
10	90	0.2613	0.2830	0.2939
20	80	0.2559	0.2749	0.2719
30	70	0.2505	0.2666	0.2746
40	60	0.2511	0.2587	0.2649

The heat capacity of premium motor spirit decreases as the volume of the additives in 100ml if the mixture increases as shown in Table 7. Understandably, aromatics have low heat content and consequently the heat output of the mixture is affected. The volume ratios of 10:90 and 20:80 showed values within the standard for benzene, toluene and BTXP mixture. All volume ratios of phenol showed values within the standard while the ratios of 10:90, 20:80 and 30:70 for xylene showed values within the standard range as shown in Table 7 and 1. As the volume of additives in 100ml mixture increases, the heat capacities of DPK decrease as shown in Tables 7.

The volume ratio of 10:90 for xylene and phenol fall within the standard range while all the values for different volume ratios of benzene, toluene and BTXP mixture showed no conformity with the standard range. Similarly, the heat capacities of AGO decrease as the volume of the additives in 100ml of the mixture increases as shown in Tables 7. The volume ratio of 10:90 for all the additives fall within the standard range as depicted in Tables 7 and 1. The other volume ratios did not meet the standard range.

3.7. Thermal conductivities

Table 8
Effect of aromatic additives on the thermal conductivity of the fractions

		PMS	DPK	AGO
Benzene ml	Fraction (ml)	W/m ^{0}C	W/m ^{0}C	W/m ^{0}C
10	90	2.0327	2.1660	2.2541
20	80	1.9575	2.1002	2.1729
30	70	1.9090	2.0343	2.0984
40	60	1.8650	1.9661	2.0160
Toluene ml	Fractions ml			
10	90	2.0072	2.1759	2.2587
20	80	1.9698	2.1421	2.1203
30	70	1.9017	2.0586	2.0556
40	60	1.8912	1.9983	2.0504
Xylene ml	Fractions ml			
10	90	2.0134	2.1822	2.2711
20	80	1.9880	2.1439	2.2070
30	70	1.9408	2.0778	2.1496
40	60	1.9287	2.0316	2.0854
Phenol ml	Fractions ml			
10	90	1.8911	2.1916	2.3307
20	80	1.9625	2.1609	2.2413
30	70	1.9635	2.1207	2.1914
40	60	1.9651	2.0797	2.1393
BTXP ml	Fractions ml			
10	90	0.0024	2.1696	2.2518
20	80	1.9635	2.1057	2.1461
30	70	1.9224	2.0598	2.1040
40	60	1.9651	1.9856	2.0343

The thermal conductivities of premium motor spirit decrease as the volume of the additives in 100ml increases. The volume ratios of 10:90 and 20:80 showed good values which are within the standard range for benzene, toluene, xylene, phenol and BTXP additives.

In DPK, the thermal conductivities decrease as the volume of additives in 100ml of the mixture increases. In other words the ability of the automotive gas oil to convey heat from one place to another decreases as the volume of aromatic additive in 100ml of the mixture increases.

The values for volume ratio of 10:90 for xylene and phenol fall within the standard range while the other ratios deviated from the standard.

Similarly, thermal conductivities of automotive gas oil decreases as the volume additives in 100ml mixture increases as shown in Table 8. The values for volume ratio of 10:90 for xylene and phenol are within the standard values while the values for other ratios did not conform to the standard.

3.8. Specific heat capacities

Table 9
Effect of aromatic additives on the specific heat capacities of the fractions

		PMS	DPK	AGO
Benzen ml	Fraction (ml)	Specific heat cap kJ/kg ^{o}C	Specific heat cap kJ/kg ^{o}C	Specific heat cap kJ/kg ^{o}C
10	90	3.56	3.42	3.41
20	80	3.37	3.30	3.28
30	70	3.23	3.17	3.16
40	60	3.10	3.04	3.03
Toluene ml	Fractions ml			
10	90	3.52	3.44	3.42
20	80	3.40	3.37	3.31
30	70	3.28	3.22	3.21
40	60	3.16	3.11	3.10
Xylene Additives ml	Fractions ml			
10	90	3.52	3.45	3.44
20	80	3.43	3.37	3.34
30	70	3.32	3.25	3.25
40	60	3.22	3.16	3.15
Phenol ml	Fractions ml			
10	90	3.50	3.41	3.49
20	80	3.34	3.27	3.29
30	70	3.20	3.13	3.12
40	60	3.05	2.99	3.08
BTXP ml	Fractions ml			
10	90	3.51	3.43	3.41
20	80	3.39	3.31	3.35
30	70	3.26	3.20	3.18
40	60	3.13	3.08	3.07

The specific heat capacity of premium motor spirit decreases as the volume of the additives in 100ml of the mixture increases as shown in Table 9. As the volume of additives in 100ml mixture increases, the specific heat capacity of DPK decreases as shown in Table 9.
The specific heat capacity of AGO decrease as the volume of the additives in 100ml of the mixture increases. These changes are as a result of low heat content of aromatic hydrocarbon which affected heat output of the mixtures.

Conclusion

From the result, it can be observed that aromatic additives can be used as improvers of physico-chemical properties of petroleum fractions. Instead of using additives which are not friendly to the environment, aromatic additives can be used because they are friendly to the environment and standard values were obtained using them.

As the volumes of additives in the 100ml mixture increase, the densities flash points, boiling points, and viscosities of the fractions increase.
Conversely, as the volume of additives increase, the degree API, thermal conductivities, specific heat capacities and heat capacities of the fractions decrease.
The best additive to petroleum fraction volume ratio was obtained as 10:90 xylene was adjudged the best additive for the fractions.

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