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Auto-Inflammation Test of Black Citric Acid Polymer (PN) and Fuel Oil (FO) Mixes - Coke Formation

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Abstract: Increasing the value of heavy oil or vacuum resides was one of the challenge of petroleum industry. It has been neglected for technology improvement because the petroleum industry has focused on lighter crude oils and their distillable liquid fractions. The great problem was its conversion yields revealed a practical maximum limits that are imposed by petroleum poly-nuclear aromatics (PNA) of the petroleum macromolecules. Our objective in this manuscript was to understand and to show the black citric acid polymers (PN) effects to the value of fuel oil. Then, we have prepared FO/PN mixes samples and tested their auto-inflammation temperature. Coke was formed and quantified by hexane and dichloromethane extraction. The results showed that not only the auto-inflammation temperature of the mixes were largely lower than the ones of fuel oil and PN but also during the mixes combustion not inconsiderable alkenes such as prop-1-ène and its derivatives non-aromatics organic compounds were formed that the rest was insoluble in hexane solvent. The PN gave an added value to the fuel oil.

Keywords: Black Citric Acid Polymer (PN), Fuel Oil, Auto-inflammation, Hexane, Dichloromethane, Soluble Coke, Insoluble Coke

1. Introduction

Black citric acid polymer (PN) was added in fuel oil to form a FO/PN mixes. The auto-inflammation temperature of mixes was tested using a kiln and porcelain crucible. A clear combustion of FO/PN mixes occurred with formation of coke deposits. Those cokes was quantified and classified using two solvents such as dichloromethane which is a polar solvent and hexane a non-polar solvent. A PN combustion mechanism was suggested and results showed that the insoluble coke affected the auto-inflammation temperature. Also, we noticed that a correlation existed between the PN's oxygen moles evolution and insoluble coke formation.

2. Auto-inflammation of Black Citric Acid Polymers (PN) and Fuel Oil (FO) Mixes

2.1. Black Citric Acid Polymers (PN) and Fuel Oil 2.1.1. Preparation of the Black Citric Acid Polymers

The first step is the dehydration of citric acid (a) molecules to obtain prop-1-ene-1, 2, 3-tricarboxylic acid (b). This reaction was catalyzed by acid catalysts like sulfuric acid [1] or metal catalysts like iron [1]. Then, these monomers combined to form 2, 3-bis(carboxymethyl)butane-1, 2, 3, 4-tetracarboxylic acid (c) which will be transformed to hydracids 2, 4, 7, 9-tetraoxooctahydrooxepino[4,
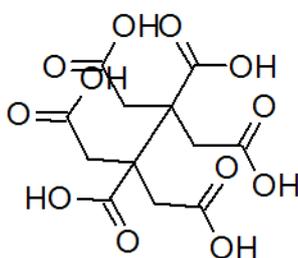
5-d]oxepine-5a, 10a-dicarboxylic acid (d) by two dehydration per molecule [1, 2]. The carboxylic acids of this last monomer was transformed to carbon dioxide at high temperature before they entered in reaction together to form polymers of citric acid. It was shown that the citric acid polymers color changed with the degree of polymerization [1]. Black was the last color which characterize the black citric acid polymer (PN) (e). (Figure 1).
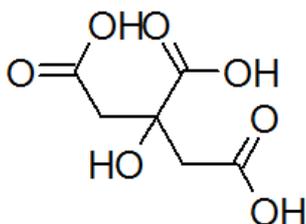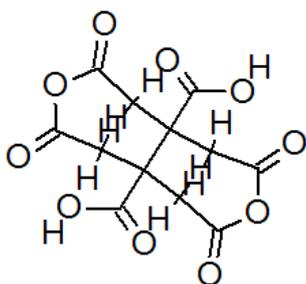

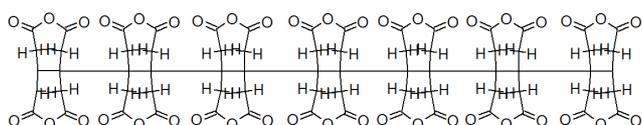(a) 2-hydroxypropane-1, 2, 3-tricarboxylic acid (citric acid)
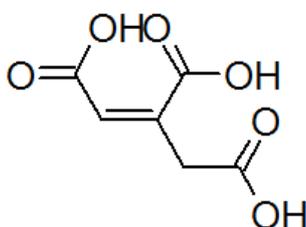
(b) prop-1-ene-1, 2, 3-tricarboxylic acid

(c) 2, 3-bis(carboxymethyl)butane-1, 2, 3, 4-tetracarboxylic acid

(d) 2, 4, 7, 9-tetraoxooctahydrooxepino [4, 5-d] oxepine-5a, 10a-dicarboxylic acid

(e) PN molecule

Figure 1. Molecules in PN formation mechanism (§ 2.1.1.).

During the PN synthesis, we used iron catalyst to synthesize PN (Figure 2) to limit the water and sulfur compounds formations which are poisons for industrial and domestic hydrocarbons' quality [3].

Figure 2. PN synthesis.

2.1.2. Characteristics of the Black Citric Acid Polymers and Fuel Oil

Table 1. PN and fuel oil Characteristics.

CHARACTERISTICS	UNITY	FUEL OIL	PN
Molecular formula		C_xH_y	$C_{70}H_{58}O_{42}$
Molecular weight	g/mol		1571.18
C weight fraction	%w/w	86.5	53.51
H weight fraction	%w/w	13.3	3.72
O weight fraction	%w/w	-	42.77
S weight fraction	%w/w	<0.2	-
N weight fraction	%w/w	$50 - 400$ ppm	-
H_2O Water	%v/v	0.15 (1 maxi)	-
Asphaltenes weight fraction	%w/w	6	-
Density	Kg/m^3	1	1.0375
Boiling point	°K	$433.15 - 1023.15$	≈573.15
Melting point	°K	403.15	339.15
Auto-inflammation point	°K	633.15	643.15
Aspect (room temperature)		viscous	crystallized
Odor		hydrocarbons	neutral
Color		Brown dark black	black

2.2. Descriptions of Equipment and Procedure Used for Auto-inflammation Temperature Determination

2.2.1. Equipment: Kiln and Crucible

To test the auto-inflammation temperature of samples FO/PN we used a kiln CARBOLITE CWF1200 (Figure 3) and a porcelain crucible (Figure 4)

Figure 3. Kiln Carbolite CWF 1200.

Figure 4. Porcelain crucible after test.

2.2.2. Procedure – Kiln Temperature Speed Neutrality

At room temperature, the fuel oil was viscous though PN was crystallized. Consequently, we carried out the fuel oil-PN mixes together in the porcelain crucible (Figure 4) from room temperature until the end of the auto-inflammation test using the kiln Carbolite CWF 1200 (Figure 3). At 573.15°K, we obtained a homogeneous liquid which remains in liquid phase even with room temperature (Figure 5). We had continued the auto-inflammation test until the temperature speed of the crucible, which was first programmed to be constant, display an abnormal variation either an increase or a reduction. The auto-inflammation is governed by oxidation reactions of the mixes. The reaction mechanism varies according to the temperature and the pressure of the reactional medium: high temperature reactional medium, average temperature reactional medium and low temperature reactional medium [4, 5]. Our test was in this last field where the oxidation phenomena are often accompanied by a heat emission chimiluminescence also called "cold flame" whose temperature is stabilized lower without inflammation of the mixes [6]. These phenomena which preceded the auto-inflammation explains the speed temperature variations temporarily without ignition of the mixes in the crucible. As a result of these observations, we record the samples' auto-inflammation temperature only if we observed a clear

ignition and explosion of the mixes fueloil-PN with appearance of coke and smoked or explosion traces on the porcelain crucible (Figure 6).

Figure 5. Homogenous liquid PN-fueloil mixes at 573.15°K
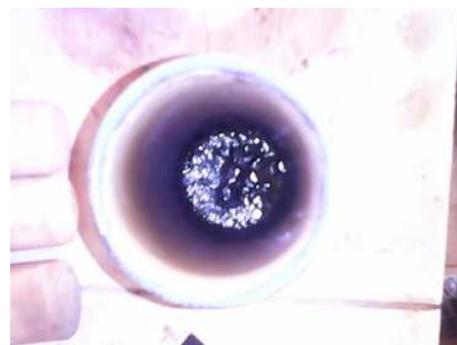

Figure 6. Coke formation, ignition and smoked or explosion traces on the porcelain crucible.

To make sure that the speed temperature programming didn't affect the exact value of the auto-inflammation temperature, we varied it by maintaining the fueloil-PN weight samples ratio to 1FO/0.5PN. We noted that the auto-inflammation value had stayed constant to be 601.15°K for the mixes sample 1FO/0.5PN. For the rest of the tests we have selected 3°C/mn the crucibles' temperature speed.
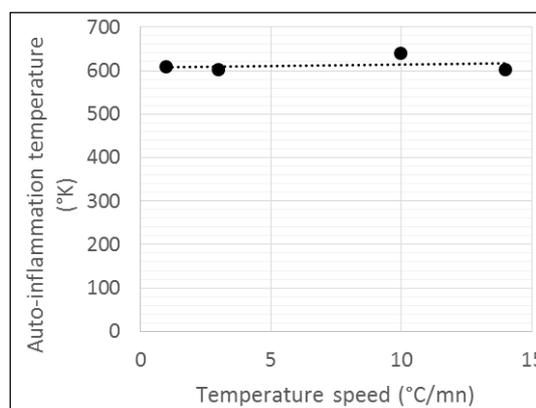

Figure 7. Evolution of auto-inflammation temperature according to crucible's temperature speed.

2.3. Results and Discussions

2.3.1. PN Effects on Auto-inflammation Temperature of the Mixes

The quantity of the PN mixed with the fuel oil was varied from zero [g] to 0.85 [g] and the fuel oil weight was maintained to be 1 [g]. We showed on table 1 with figure 8 the results of the auto-inflammation temperature of the mixes.

Table 2. PN effects on auto-inflammation temperature of the mixes.

PN Ratios of mixes (gFO/gPN)	1PN	1FO/0.3PN	1FO/0.5PN	1FO/0.66PN	1FO/0.85PN	1FO
Auto-inflammation temperature (°K)	643.15	603.15	601.15	608.15	618.15	633.15
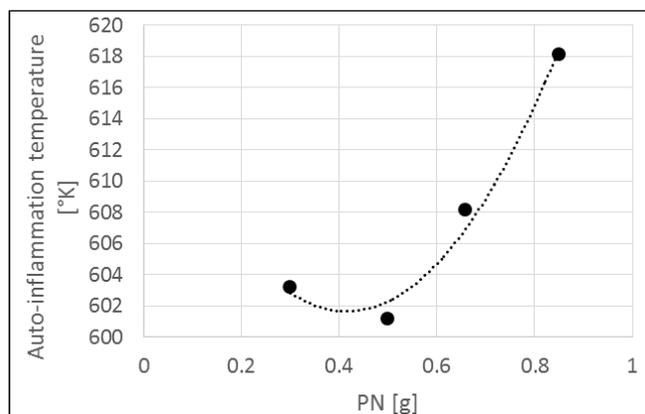
Figure 8. Evolution of auto-inflammation temperature according to PN weight.

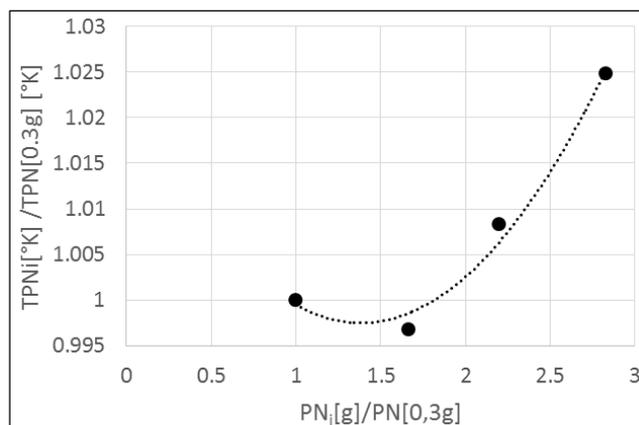*Figure 9. Evolution of the auto-inflammation temperature variation with the weight of PN variation in comparison with auto-inflammation temperature and weight at the ratio 1FO/0.3PN.*

This test of auto-inflammation temperature for fuel oil-PN mixes was classified among low temperature reactional medium [5]. The reaction mechanism of the auto-inflammation phenomena was characterized by hydrocarbon oxidation with molecular oxygen in the air to form peroxides radicals (RO_2) which was decomposed to aldehydes (R'CHO) and carbon monoxide (CO). Then, R'CHO gave carbon monoxide CO which were oxidized by air oxygen to form carbon dioxide (CO_2) and H_2O with release of energy [7, 8] (Figure 13). That is why, the presence of PN reduce the auto-inflammation temperature of every mixes lower than auto-inflammation temperature of PN (643.15°K) and fuel oil (633.15°K) (table 2). To confirm the transformation of PN and PN's Oxygen atoms to aldehydes and alkenes (prop-1-ène – figure 11) then carbon monoxides and their participation during the combustion we have plotted the auto-inflammation temperature variation in comparison with auto inflammation temperature for 1FO/0.3PN (603.15°K) according to the weight variation of PN in comparison with the weight of PN for 1FO/0.3PN (0.3g) (figure 9). More there was PN, more the oxidation of (R'CHO) need energy to form R'CO. and $H_2O^.$ [8], consequently, the auto-inflammation temperature increased without exceeding the auto-inflammation combustion of PN pure and fuel oil pure because the decomposition R'CO. and the oxidation of CO are exothermic reactions [9] and more there were PN more there were R'CO. and CO to be oxidized than fuel oil pure.

2.3.2. PN's Oxygen Atoms Effects on Auto-inflammation Temperature of the Mixes

Table 3. PN's Oxygen atoms effects on auto-inflammation temperature of the mixes.

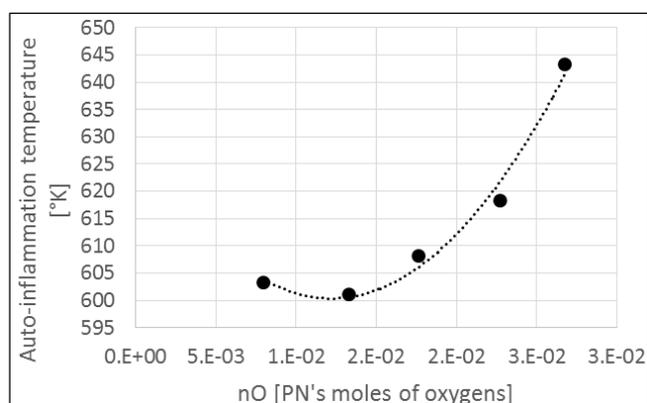| PN Ratios of mixes (gFO/gPN)	PN's oxygen atoms ($\times 10^{-3}$ moles)	Auto-inflammation temperature (°K)
1PN	26.754	643.15
1FO/0.3PN	8.022	603.15
1FO/0.5PN	13.356	601.15
1FO/0.66PN	17.64	608.15
1FO/0.85PN	22.72	618.15
1FO	-	633.15

Figure 10. PN's oxygen effect on auto-inflammation temperature of mixes.

We showed in the table 2 and figure 10 the effects of the

oxygens atoms to the auto-inflammation temperature. They confirmed that more there were PN's Oxygen atoms, the auto-inflammation temperature of the mixes increased

because of the transformations of the oxygen to aldehyde and alkenes (prop-1-ène) which are endothermic reactions before their combustions (figure 11) [8].
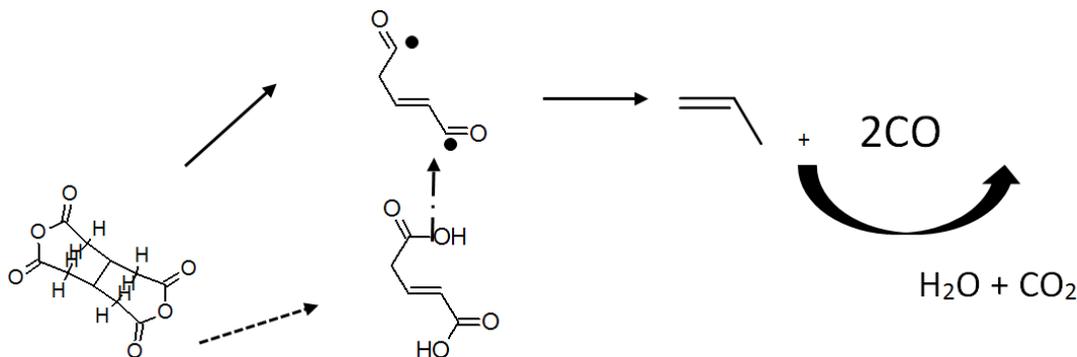

Figure 11. Streamlined mechanism of PN's monomer combustion [8].

3. Auto-inflammation's Coke Analysis

After each auto-inflammation tests, coke remains in the porcelain crucible (Figure 6). We weighted the coke and compared it with the initial weight of the mixes. We deduced the coke percentage in comparison with the mixes. Also, we have studied the coke's nature, then we have tried to deduce some conclusions in comparison with auto-inflammation temperature.

3.1. Description of Coke Extraction

3.1.1. Equipment: Scales and Solvents

For the coke extraction [10], we used two solvents, a polar solvent aprotic the dichloromethane, a non-polar solvent hexane, and a scale to weight the coke insoluble. We saw in the following table the solvents' characteristics (Table 4) [11].

Table 4. Dichloromethane and hexane characteristics.

Solvent	Dichloromethane	Hexane
Formula	CH_2Cl_2	C_6H_{14}
Boiling point (°C)	40	69
Permittivity	9.1	1.88
Density (g/ml)	1.326	0.655
Dipole moment	1.60	0.00

3.1.2. Procedures

We have taken a few sample of coke. We put it in the first solvent, dichloromethane. A part of the coke composed largely of aromatics and poly-nuclear aromatics (PNA) less than 5 rings aromatics [12] or PN and derivatives is soluble in DCM and another part was insoluble. We filtered the solution with a filter paper and take in the color of the soluble coke. The insoluble coke was retained on the filter paper that one dries in a beaker heated with a temperature around 373°K during a few minutes. Dried insoluble coke is transvased in a crystallizer beforehand tared and the unit is weighed. We thus obtained the weight of DCM coke insoluble.

Another few sample of coke was taken. We put it in the second solvent, hexane which is non-polar. A part of the coke composed of PNA poly-nuclear aromatics more than 5 rings such as PNA_6 and PN or PN's derivatives was insoluble in hexane and another

part composed of non-aromatics or light hydrocarbons or linear hydrocarbons was soluble in hexane. We filtered the solution with a filter paper. The insoluble coke was retained on the filter paper that one dries in a baker heated with a temperature around 373°K during a few minutes. Dried insoluble coke is transvased in a crystallizer beforehand tared and the unit is weighed. We thus obtain the weight of hexane coke insoluble.

3.2. Soluble and Insoluble Coke Identification

3.2.1. Soluble Coke

Dichloromethane is a polar solvent aprotic which can extract aromatics such as PNA_4 less than 5 rings aromatics [10, 12] and little oxygenated alkene compounds such as PNA_4-(2E)-pent-2-enedioic acid or just (2E)-pent-2-enedioic acid (figure 11) [11] whereas hexane is a non-polar solvent which can extract hydrocarbons like fatty acid, alkane, alkenes and non-aromatic compound [11].

Table 5. Probable organic compounds coke soluble in dichloromethane and hexane.

SOLVENTS	SOLUBLE COKE	
Dichloromethane	PNA_4	PNA_4-(2E)-pent-2-enedioic acid
Hexane	Alkane Alkenes and non-aromatic coke precursors	

3.2.2. Insoluble Coke

Insoluble coke was obtained by soluble coke aromatization [10] and composed largely by poly-nuclear aromatics more than six rings aromatics [12]. Eventually those last poly-nuclear aromatics with the rest of black acid citric can form PNA_6-[PN].

Table 6. Probable dichloromethane and hexane organic compounds and coke insoluble.

SOLVENTS	INSOLUBLE COKE		
Dichloromethane	PNA_6	PNA_6-(2E)-pent-2-enedioic acid	PNA_6-[PN]
Hexane	PNA_6	PNA_6-(2E)-pent-2-enedioic acid	

We saw that insoluble coke in dichloromethane was obtained by its soluble coke aromatization [10].

$$PNA_4 \longrightarrow PNA_6$$

$$PNA_4\text{-(2E)-pent-2-enedioic acid} \longrightarrow PNA_6\text{-(2E)-pent-2-enedioic acid}$$

$$PNA_6 + PN \longrightarrow PNA_6\text{-PN}$$

$$3C_3^= \longrightarrow C_9^= \longrightarrow \text{Aromatics (by Oligomerization reaction)} \longrightarrow PNA_4$$
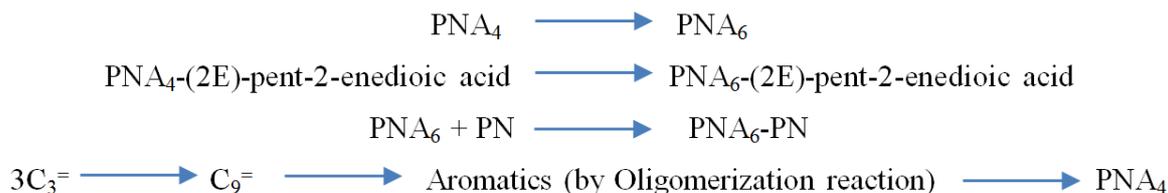
Figure 12. Soluble and insoluble coke formation mechanism.

3.3. Results and Discussions

We showed in the following table the results of coke extraction with dichloromethane and hexane according to the mixes samples.

Table 7. Coke extraction with dichloromethane and hexane according to the mixes samples.

	PN	1FO/0.3PN	1FO/0.5PN	1FO/0.66PN	1FO/0.85PN	FO
Coke total (%)	70	72.58	40.67	48.79	52.32	71
Insoluble coke CH_2Cl_2 (%)	83.33	27.77	50	50	63.88	98
Soluble coke CH_2Cl_2 (%)	16.67 (uncolored)	72.23 (black)	50 (black)	50 (brown)	36.12 (black)	2% (brown)
Insoluble coke hexane (%)	75	27,78	85	80.55	47	96
Soluble coke hexane (%)	25	72,22	15	19.45	53	4

Whatever the proportion in PN, the coke obtained after auto-combustion tests were always largely lower than the coke formed by PN alone and FO alone. These results showed that the PN contributed to the combustion of the mixes FO/PN. Noticed nevertheless that for 1FO/0.3PN the coke total was 72.58%, it was composed for a large part by the soluble coke in dichloromethane (72.23%) and confirm his lower auto-inflammation temperature (603.15°K) (Figure 13). The insoluble coke which is one of the poison of combustion mechanism was only 27.77% [12]. To confirm the insoluble coke and total coke effects on auto-inflammation temperature, we plotted it in the following figure 12 and figure 13. We remarked also differences between insoluble coke in CH_2Cl_2 and insoluble coke in hexane (8.33% -PN) (16.8%-1FO/0.85PN). According to the table 7, those values confirmed low direct participation of PN to the insoluble coke formation. They was first cracked. Then, the cracking products, which were soluble in hexane such as propene oligomerization products [10], formed aromatics and soluble coke [10]. Then, soluble coke gave insoluble coke.

We have noticed that hexane soluble coke of the mixes were all the time superior to the FO hexane soluble coke. It was 53% at the mixes 1FO/0.85PN. So, hexane insoluble coke decreased and the coke quantity of mixes was lower than PN's and FO's coke quantity (Table7). We can conclude that the presence of PN improved the light hydrocarbons production such as alkanes, alkenes (propene) and non-aromatics hydrocarbons of the mixes FO/PN (figure 11).

It's very interesting because the PN's molecules not only improved the quality of the FO/PN mixes during the auto-inflammation test by producing those hexane soluble coke precursors (table 5) but also decreased the initial coke quantity of the FO (Figure 14).
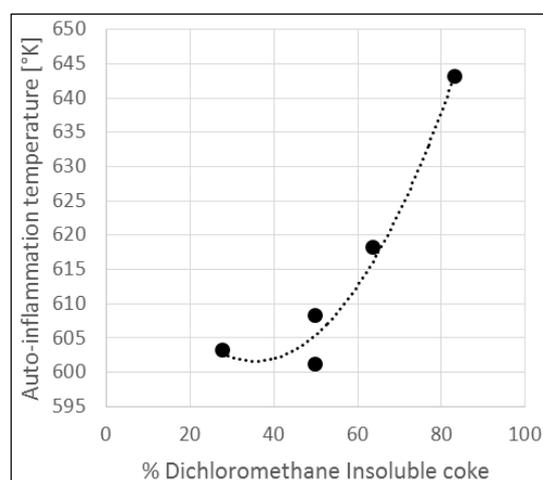

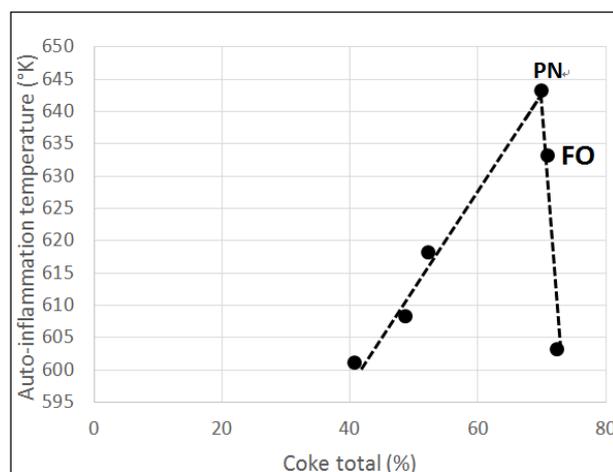*Figure 13. Auto-inflammation temperature according to dichloromethane insoluble coke.*

Figure 14. Auto-inflammation temperature according to coke total percentage.

3.3.1. PN Effects on Coke Formation and Auto-inflammation Temperature of Mixes

We have confirmed that insoluble coke is the principal responsible of auto-inflammation temperature augmentation. We plotted in the following figure (Figure 15) the correlation between the insoluble coke and the PN quantity. We saw that the insoluble coke increased with the PN quantity.
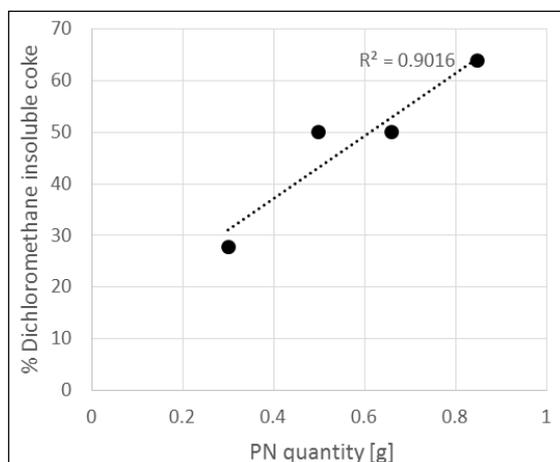

Figure 15. Dichloromethane insoluble coke according to PN quantity of the mixes.

3.3.2. Effects of PN's Oxygens and Hydrogens Atoms on Insoluble Coke Formation and Auto-inflammation Temperature of Mixes

The PN's oxygen weight percent was 42.77%, it's interesting to study its influence to the insoluble coke formation. The literature said that the presence of heteroatoms and hydrogen influence the coke formation particularly insoluble coke formation [12, 13]. The following figures showed clearly and confirmed those information (Figure 16 – Figure 17). Whereas, we noticed that PN's oxygen didn't took part directly to the coke formation (c. f. §3.3.) but their combustion (Figure 11) gave more energy to the insoluble coke formation reaction and cracking reaction. That is why, the presence of PN reduce the auto-inflammation temperature of every mixes lower than auto-inflammation temperature of PN (643.15°K) and fuel oil (633.15°K) (table 2).
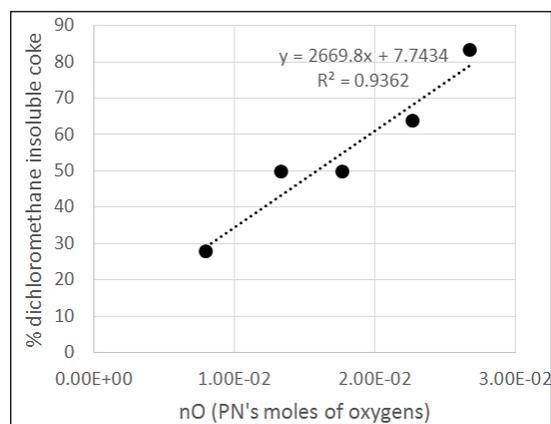

Figure 16. Dichloromethane insoluble coke according to PN's oxygens moles in the mixes.
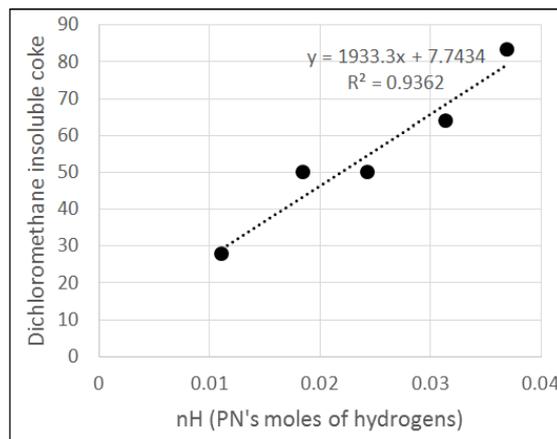

Figure 17. Dichloromethane insoluble coke according to PN's hydrogens moles in the mixes.

4. Conclusion

The PN molecule is an efficient additive to improve the quality of the fuel oil and its added value. The presence of not inconsiderable quantity of oxygen in PN's molecule, the clear formation of prop-1-ène and his derivatives alkenes and non-aromatic compounds during its combustion and finally the real diminution of the mixes' coke quantity in comparison with FO's coke quantity took us also to say that PN can be an efficient additive to heavy oil and why not to vacuum resides before their upgrading process. Being also given that innovations were made to have more complete combustion to fuels used in diesel engines such as the compression which can reach 2000 bar with a temperature carried over 873°K (largely higher than auto-inflammation temperature of FO/PN samples), we think that it's interesting to test and to use the FO/PN mixture like fuel to industrial engines, to boat engines and to boilers.

Acknowledgements

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