

ASPECTS CONCERNING THE FORMING INHIBITING OF THE DEPOSITS IN GASOLINES

NICULAE ANA DANIELA^{1*}, PETRESCU MARIUS GABRIEL²,
GEORGESCU OVIDIU³, GEORGESCU LUCIAN⁴, BUCUROIU RODICA²

¹*IPIP Ploiesti,*

²*Petroleum-Gas University of Ploiesti,*

³*SC GEXACOR SA Ploiesti,*

⁴*George Barițiu University of Brasov*

Abstract: This paper presents results of research on the process of forming gums in gasoline resulted from the pyrolysis of the ethane composition: propane, in a proportion of 1 : 3 in weight, at a temperature of 820⁰C. In addition, it has been researched the thermal stability of these inhibitors by the thermo-gravimetric analysis (TGA). From the TGA thermo-grams, there were appreciated the temperatures of the losses in weight during the heating process. It was found that the presence of inhibitors does not prevent from the formation of the peroxide radicals, but it prevents from their initiation of the reaction chains. The phenols efficiency is improved by alkylation in the positions 2, 4 and 6. The good results are obtained for the substitutes in all the three positions with a methyl group in para and at least a group of t-butyl in position orto comparing with the hydroxyl.

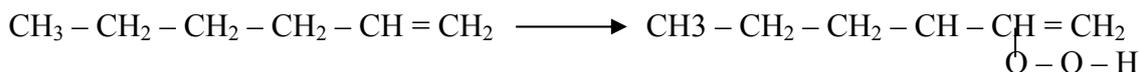
Keywords: gasoline, pyrolysis, inhibitors.

1. INTRODUCTION

The gasoline that derives from the pyrolysis of the volatile hydrocarbons in order to obtain ethylene and propene has in its composition alkenes with linear and branched chain, bi-alkenes, cyclic alkenes and aromatic hydrocarbons. Because the unsaturated and the aromatic hydrocarbons prevail, the gasoline in contact with the oxygen presents pronounced chemical instability and may form even in the deposit normal conditions important gum quantities that affect the further working and capitalization processes. Oxidation stability is influenced by storage temperature, long residence times, access and availability of oxygen, the catalytic influence of solids such as rust particles and presence or absence of inhibitors [1-3].

The olefins oxidant characteristics due to certain peroxides resulted from the addition of certain oxygen molecules to the olefin junction. The self – oxidation, in the presence of the oxygen molecules, takes place at normal temperature. The primary product in any self – oxidation reaction is a hydro-peroxide [4].

* Corresponding author, email georgescu_ana2002@yahoo.com



Hexane (1)

Hydro-peroxide of 1-hexane-3-il

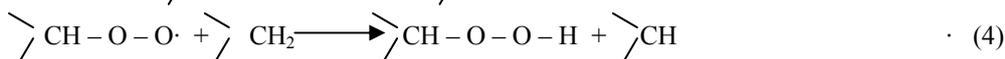
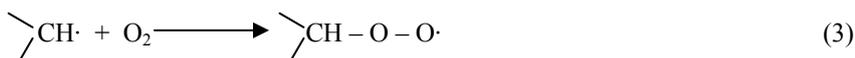
The kinetic research showed that the most self – oxidations are chained self – catalyzed reactions, meaning accelerated by the self-reaction product. The self – oxidations are initiated by promoters, meaning substances that engender certain free radicals by thermal decomposition. Such a promoter is the benzyl peroxide.



The free radical, the initiator of reaction chains, extracts a hydrogen atom from the CH or CH₂ group the most reactive from the molecule (CH₂ allyl group, in the case of the olefins):



In this way, a free radical of the olefin comes into being. This is combined with an oxygen molecule engendering a free radical of the hydro-peroxide able to extract a hydrogen atom from a new olefin molecule:



The (3) and (4) reactions, are reiterating many times, constituting the so – called the reactions chain (2) $\text{>CH}\cdot \longrightarrow \text{>CH} - \text{CH}\cdot$.

The interrupting reactions take place by combining two radicals or by the action of an inhibitor.

The inhibitors yield easy an hydrogen atom to the free $\text{>CHOO}\cdot$ radical, transforming in poor energy free radicals that could not initiate reactions chains or that combine with this radical giving peroxides [4]. These substances with inhibition action are in principal derivates of aminophenol, phenylene – diamine or alkylate phenols in more positions. By modern techniques, such as spectroscopy in infra – red or nuclear magnetic resonance it may be measured the kinetic and physical parameters of the researched system in a very short time [5, 6].

2. THE EXPERIMENTAL PART

It has been researched the process of forming gums in gasoline resulted from the pyrolysis of the ethane composition: propane, in a proportion of 1 : 3 in weight, at a temperature of 820 °C. The gasoline was been characterized by gas chromatography and the obtained results are presented in the Table 1.

Table 1. The researched gasoline composition.

No.	Name of the compounds	% g
1	Butane, butene, pentane, pentene	20,57
2	Isoprene	5,06
3	Piperilene	9,55
4	Cyclo-pentadiene	4,10
5	C ₆ – C ₇	2,80
6	Benzene	28,8
7	C ₉	0,07
8	Toluene	3,62

9	C ₁₀ + xylenes	3,24
10	Di-cyclo-pentadiene	18,82
11	Heavy compounds	3,37

From these data, it is been deduced that the pyrolysis gasoline of the C₂ – C₃ fraction composition has an increased content of unsaturated hydrocarbons able to polymerize in gentle conditions, in the presence of the oxygen, determining the gums formation.

The oxygen solubility measured at 25⁰C and having a pressure of 1 bar varies in terms of the hydrocarbon nature (Table 2) [7].

Table 2. The oxygen solubility in hydrocarbons.

No.	Hydrocarbon's type	Solubility ppm	No.	Hydrocarbon's type	Solubility ppm
	Paraffines			Naphthenes	
1	Pentane	118	8	Cyclohexane	76
2	Hexane	101	9	Methylcyclohexane	83
3	Heptane	90	10	Cyclooctane	54
4	Octane	89		Aromatic	
5	Decane	68	11	Benzene	61
6	Do-decane	54	12	Toluene	67
7	Pentadecane	41	13	Paraxylene	71

For the inhibition of the deposits forming in the pyrolysis gasoline there were used 3 types of inhibitors:

- **Inhibitor A** on the base of 2,2'-methylene-bis(6-(1-methylcyclohexile)-p-cresol);
- **Inhibitor B** on the base of N-isopropyle-N'-phenyl-p-phenylen – diamine;
- **Inhibitor C** on the base of 2,4-dimethyl-6-thirdbutylphenole; 4-methyl-2,6-dithirdbutylphenole and other alkylphenoles with big activity of anti - oxidants.

There were made solubility tests of these inhibitors in pyrolysis gasoline, toluene and benzene, the results being presented in the Table 3.

Table 3. The solubility of the tested inhibitors.

No.	Inhibitor's name	Solubility in		
		Pyrolysis gasoline	Toluene	Benzene
1	Inhibitor A	soluble	soluble	soluble
2	Inhibitor B	soluble	soluble	soluble
3	Inhibitor C	miscible	miscible	miscible

In addition, it has been researched the thermal stability of these inhibitors by the thermo-gravimetric analysis (TGA). From the TGA thermo-grams, there were appreciated the temperatures of the losses in weight during the heating process.

The A, B and C inhibitors were tested in pyrolysis gasoline in the concentrations field of 25 – 400 ppm. The test was made according to the ASTM 525 – 95 method, in oxygen atmosphere at a pressure of 7 bar and the inhibitor's efficiency was appreciated by the dimension of the induction period.

3. RESULTS AND DISCUSSIONS

In the Figure 1 there are presented the losses in weight for the inhibitors used with the temperature increase.

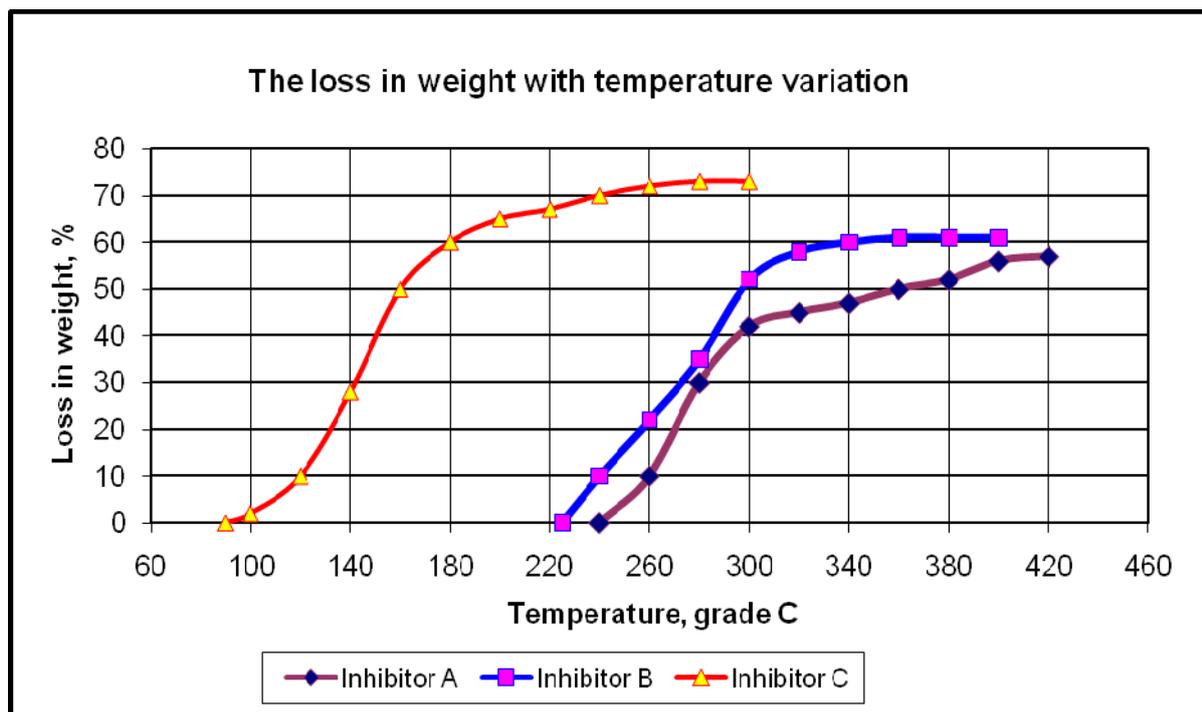


Fig. 1. The loss in weight with temperature variation of the tested inhibitors in pyrolysis gasoline.

Table 4. The variation of the induction period with the concentration of the inhibitors tested in the pyrolysis gasoline.

No.	Inhibitor	Conc., ppm	Period of induction, min.	No.	Conc., ppm	Period of induction, min.
1	A	25	40	6	250	115
2		50	70	7	300	117
3		100	90	8	350	119
4		150	95	9	400	120
5		200	105	10	450	120
11	B	25	70	16	250	170
12		50	105	17	300	185
13		100	125	18	350	195
14		150	138	19	400	205
15		200	155	20	450	210
21	C	25	30	26	250	100
22		50	40	27	300	110
23		100	60	28	350	117
24		150	78	29	400	125
25		200	90	30	450	126

From the presented thermo – grams analysis it results that the A and B inhibitors have an initial loss in weight temperature of 240°C, respectively 225°C. The best thermal stability has the A inhibitor on the basis of 2,2'-methylene-bis(6-(1-methylcyclohexyle)-p-cresol).

In the Table 4 there is presented the variation of the induction period with the concentration of the inhibitors tested in the pyrolysis gasoline.

From the data resulted in the Table 4 it has been found that the best results were obtained with the B inhibitor that has in its composition N-isopropyl-N'-phenyl-p-phenylen-diamine. The A and C inhibitors assure the

inhibition of the pyrolysis gasoline in the studied concentrations field, but at smaller values than those of the B inhibitor. By realizing the composition of the inhibitors B : C in proportion of 1 : 1 and by its testing in the pyrolysis gasoline it has been found that its synergetic effect (Figure 2) as against each inhibitor. Thus, the synergetic composition has an induction period of 95 minutes to a concentration of 25 ppm; 152 minutes to 100 ppm; 220 minutes to 300 ppm and 230 minutes to 450 ppm, meaning it is bigger with 10 – 26 % than that of B inhibitor and with 18 – 77% than the C inhibitor. The presence of inhibitors does not prevent from the formation of the peroxide radicals, but it prevents from their initiation of the reaction chains. Antioxidants do not chemically consume oxygen but disrupt the chain reactions by combining with peroxides and free radicals in the liquids, thus neutralizing their potential to initiate the chain reactions mentioned [7].



The phenols efficiency is improved by alkylation in the positions 2, 4 and 6. The good results are obtained for the substitutes in all the three positions with a methyl group in para and at least a group of t-butyl in position orto comparing with the hydroxyl.

4. CONCLUSIONS

From the made researches it results the following main conclusions:

1. The forming of the polymers in the pyrolysis gasoline results from a radical mechanism in which the essential role has the apparition of the peroxides and of the hyper-peroxides resulted from the self – oxidation of the hydrocarbons at a normal temperature under the influence of the atmospheric oxygen.

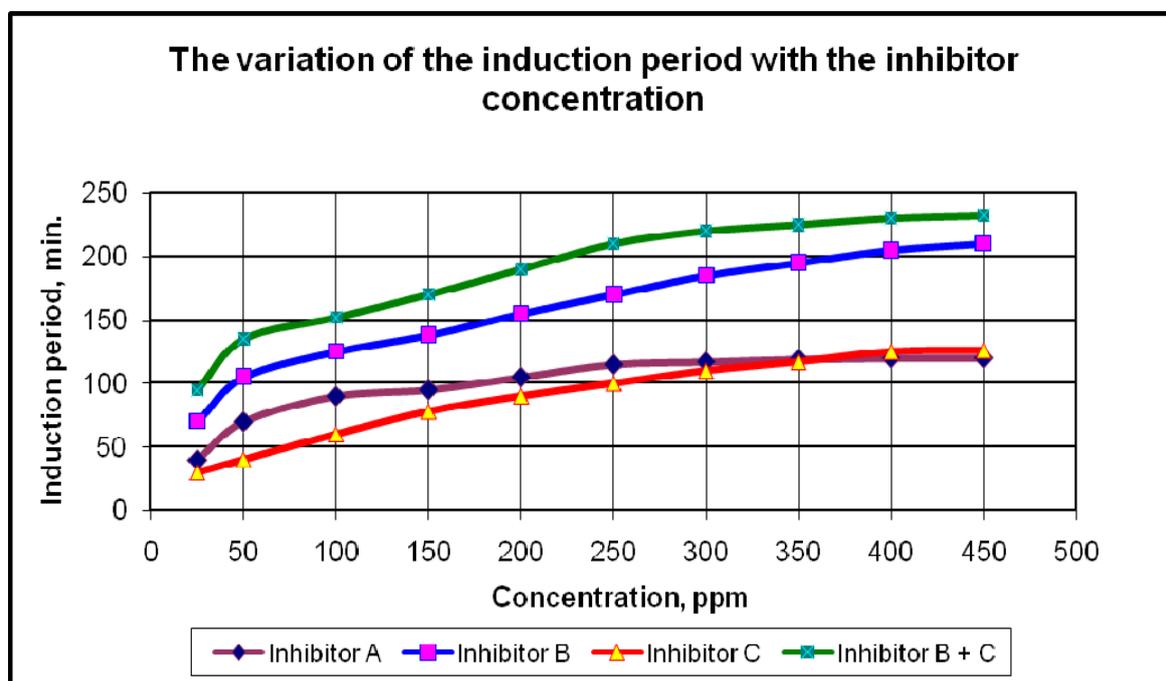


Fig. 2. The variation of the induction period with the concentration of the synergetic composition B+C in pyrolysis gasoline.

2. The self – oxidation reactions of the unsaturated hydrocarbons and those of polymerization that accompany are prevented or delayed by the addition, in small quantities, of some substances with inhibition action or anti – oxidants.
3. The testing of the three types of inhibitors (A, B and C) emphasized the possibility of their use in pyrolysis gasoline in order to inhibit the oxidation and polymerization processes in satisfactory conditions.
4. The B inhibitor on the basis of N-isopropyl-N'-phenyl-p-phenylen - diamine assures a good inhibition of the pyrolysis gasoline.
5. The synergetic composition of the inhibitors B:C, on the base of N-isopropyl-N'-phenyl-p-phenylen - diamine, respectively 2, 4-dimethyl-6-thirdbutyl phenol and 4-methyl-2, 6-dithirfbutylphenol in a proportion of 1 : 1 assures a superior inhibition of the pyrolysis gasoline in comparison with the individual inhibitors.

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