EFFECT OF SOME ADDITIVES ON GUM FORMATION IN PLASTIC DERIVED DIESEL (PLASTODIESEL) IN MIXTURE WITH DIESEL B10 TERPEL

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ABSTRACT

The results of the assessment of some additives on the formation of gum in Plastic derived Diesel DPC, mixed with conventional Diesel Terpel B10, are summarized in this paper.

Keywords

Diesel, Oxidation Stability, Gum Formation, Additives

1. INTRODUCTION

The production of vehicular fuels from waste plastics, is a task that have been undertaken in recent years by several companies worldwide such as Cynar in England, Agylix in USA, Diesoil in Switzerland, Blest Co. in Japan, JBI Plastic to Oil in New York and many others in various countries, with varying degrees of technological development and scientific depth.

During the pyrolysis process it is produced a mixture or cocktail of hydrocarbons with different boiling points, which generally is not suitable for direct motor use because their properties do not meet the required specifications for this use, among others, the Pour Point, the Cloud Point, the Cold Filter Plugging Point (CFPP), the Flash Point, the Initial and Final boiling temperature and the content of residual carbon (Conradson Carbon or Micro Carbon Residue).

Even though fractional distillation allows for cuts that adjust and meet most of the properties required in vehicle fuels, the same does not guarantee their quality because some of its properties such as their oxidation stability is beyond the control of any distillation system.

Besides the above, fuels derived from pyrolysis of plastics, by the very nature of the thermal cracking process and/or catalyst, contain a lot of double bonds, which makes them unstable over time, with a tendency to repolymerization and Gums formation.

This, coupled with the presence of oxygen in the products, which is introduced into the process as a contaminant biomass as food waste or paper present in processed wraps, increases the instability of fuel and the tendency to the formation of gums , resulting in soiling valves in gasoline engines and obstruction of the filters and the injection systems of diesel engines.

So far we have not seen any company that marketed worldwide Vehicular fuels as Diesel derived from pyrolysis of Plastic and even less gasoline for vehicles.

Gum formation in gasoline, as compared to Diesel, is slightly more damaging to the engine operation due to the way the engine uses the fuel through the carburetor or by an injection system into the intake manifold, while in diesel engines it is directly injected into the cylinder or in some cases to precombustion chambers, in which process the formation of gums is less problematic than in the case of gasoline engines.

In order to contribute to the solution of this problem, the aim is to evaluate the effect of some additives on gum formation (Susceptibility to oxidation) of the diesel derived from the pyrolysis of plastics waste in mixtures with conventional diesel fuel (B10) in Colombia, more specifically in the City of Bogotá DC

2. MATERIALS AND METHODS

2.1. Plastic Derived Fuel

The Diesel fuel derived from plastic, hereinafter called Pastodiesel or DPC Diesel, used in this test was produced by a distillation cut of Plastic pyrolytic oil, here called Crude Plastic Oil, conducted between 240 ° C and 360 ° C at a pressure of 560 mm Hg on a giant rotary evaporator (ca. 300 liters capacity), heated by direct gas (LPG) flame, equipped with a small rectification tower with an equivalent height of two theoretical plates and a water-cooled condenser. The DPC Diesel fuel was produced between June and September/2015 and it was stored from September/2015 until August/2016 in a sealed stainless steel 304 tank, without air access. The distillation curve and other properties of this Diesel DPC can be seen in the following table:

ANÁLISIS DE COMBUSTIBLES

Dr. Calderón LABS

Curva de Destilación ASTM D 86

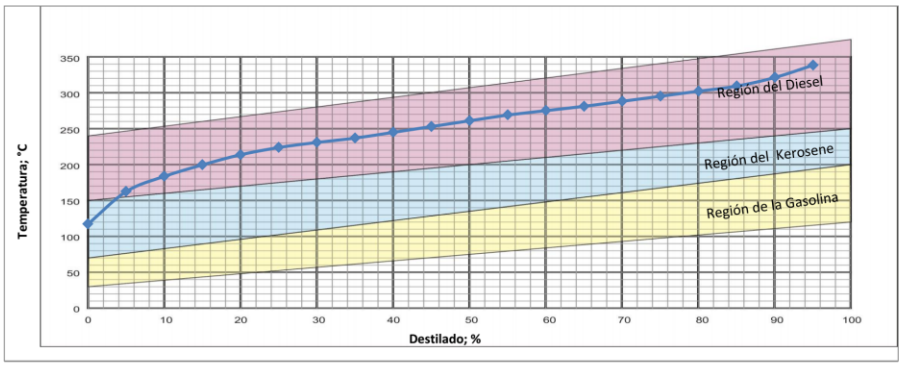
Fecha: 17 de junio de 2015
Analisis de Combustibles No.: AC-129
Muestra: Diesel de 1a Destilación en Planta
Cliente: Dr. Calderón Labs

	Temperatura	Hora	Observación
	28	1:53:00 p. m.	
Volumen			
0	120	2:00:00 p. m.	
5	165	2:01:00 p. m.	
10	186	2:03:00 p. m.	
15	202	2:04:00 p. m.	
20	216	2:05:00 p. m.	
25	226	2:05:00 p. m.	
30	233	2:06:00 p. m.	
35	239	2:07:00 p. m.	
40	247	2:08:00 p. m.	
45	255	2:08:00 p. m.	
50	263	2:09:00 p. m.	
55	271	2:09:00 p. m.	
60	277	2:10:00 p. m.	
65	283	2:11:00 p. m.	
70	290	2:11:00 p. m.	
75	297	2:12:00 p. m.	
80	304	2:12:00 p. m.	
85	311	2:13:00 p. m.	
90	323	2:14:00 p. m.	
95	340	2:15:00 p. m.	Taponamiento Parafínico

Peso Lleno; g	129
Peso Vacio; g	48
Volumen;ml	100
Densidad; g/ml	0.810
Peso Final; g	49
Residuo; g	1
Temp Inicial; °C	28
Parafina en Cond.; g	1

Densidad Relativa 15,6/15,6° C	**0.810**
Grado API; ° API	**43**
Viscosidad a 40°C; cSt.	
Flash Point; ASTM D-93; °C	**> 25**
Flash Point; ASTM D-93; °C	**75**
Pour Point; ASTM D-97-08; °C	**<-6**
Cloud Point; ASTM D-2500-05; °C	**5**

Indice de Carcaterización, Kuop;		
Temperatura Media Ponderada en Volumen		
TMPV; °C	246.50	
TMPV TBP; °C	251.33	
Kuop		**12.07**
Escala Kuop;		
10 Aromático; 11 Nafténico; 12 Mixto; 13 Parafínico		



Región del Diesel
Región del Kerosene
Región de la Gasolina

Observaciones:
Crudo con Poliestireno
Olor Ligeramente Aromático.

Felipe Calderón Sáenz
Director General

Fig. 1. Distillation Curve for Diesel DPC, at Atmospheric pressure in Bogotá at 560 mm Hg.

2.1. Conventional Fuel Diesel B10

Conventional Diesel Fuel B10 used in this test was obtained in Terpel Service Station, Calle 68 x Cra. 29 Bogotá D.C., in the month of July 2016

2.2. Equipment for measuring the oxidation susceptibility.

The equipment used for these tests was inspired following the methodology and procedures described in ASTM D-2274-14 standard with some variants we describe below.

	ASTM 2274	Ensayo No. 7
Temperatura de la prueba; °C	95	90
Tiempo de la Prueba; hr	16	24
Tiempo de Maduración; días	0	15
Cantidad de Muestra en la Prueba; ml	350	500
Gas Circulante;	Oxígeno	Aire
Caudal; lt/hr	3	60
Mateiral del Condensador y tubo de Inyección del Gas;	Vidrio	Ac. Inox 304
Temperatura de Secado de las Gomas; °C		70
Tiempo de Secado de las Gomas; hr		60
Solvente para lavar los Insolubles:	IsoOctano	Varsol
Solvente para las Gomas Solubles:	Trisolvente	Thinner

Below is a view of the equipment showing the fuel volume used in this test:

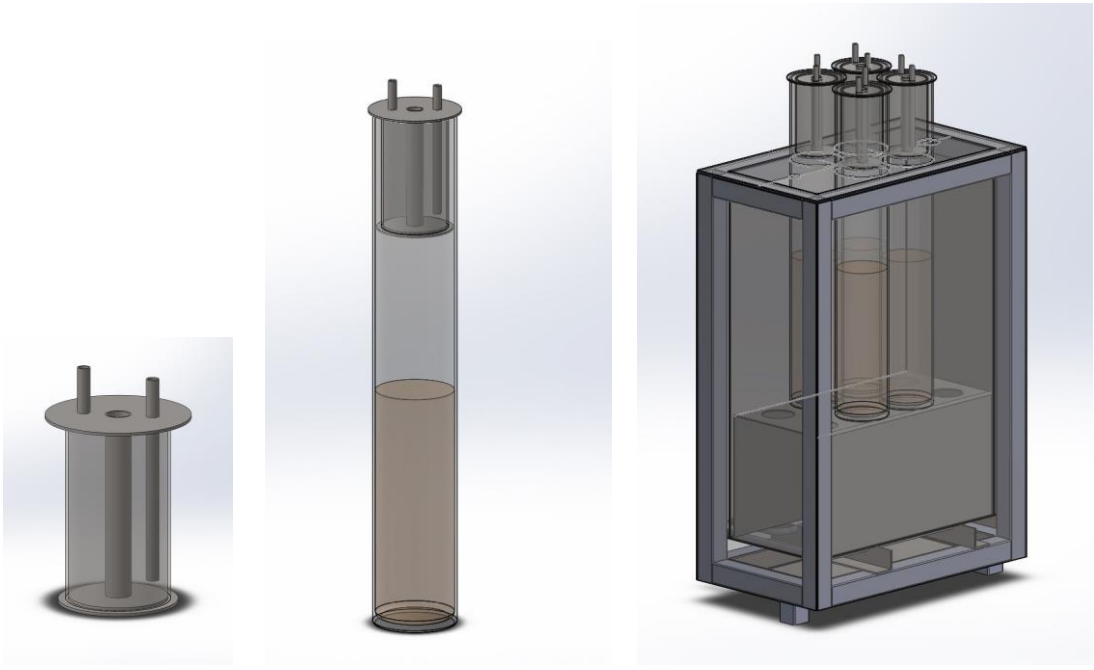


Fig. 2. Equipment used in this test; a) Condenser; Stainless Steel 304; b) Glass tube and condenser; c) Thermal bath for 4 tubes.

Fig.3. Equipment during the test. a) thermal bath, b) Pressure Filter

2.3. Filtration Equipment.

One pressure Filter was built in structural stainless steel 304 tube, 2.5" diameter, with a net filtration area of 28.27 cm2 and a total height of 17.68 cm for filtration of the solid gum deposited. The gums were filtered by means of a disk of qualitative rapid filter paper, 68 mm diameter.

2.4. Used Treatments

The mixtures used in this test were conducted by volume with the following proportions:

Combustible a Utilizar en todas las muestras: Mezcla 50/50			
	Aditivos	Ref.	Dosis
			uL/L
1	Orco	DKC-3468-XCH	1000
2	Simoniz	Qualitor	3120
3	ACPMax		2462
4	Testigo Absoluto		0

The test was mounted the September 27, 2016 at 6 PM. The tubes in the bathroom were withdrawn on September 28 at 6 PM and allowed to stand at room temperature in the shade for 15 days, until 13 October 2016

3. RESULTS AND DISCUSSION

The test was running normally and at the end thereof, it was realized the following observations:

September 28/2016 7.00 PM
Trat No. 1. Very Light Haze
Trat No. 2. without Haze
Trat No. 3. Slight Haze in the liquid, Ring in the glass and Visible Precipitate in the bottom.
Trat No. 4. Slight Haze in the liquid, Ring in the glass, Visible Precipitate in the bottom and a precipitate on the air pipe

October 13/2016 7.00 PM
Trat No. 1. Very Slight Haze and slight precipitate.
Trat No. 2. Intense Haze (although very thin as it pass the filter) and slight precipitate.
Trat No. 3. Liquid without Haze, Ring in the glass and large Visible Precipitate in the bottom.
Trat No. 4. Liquid without Haze, Ring in the glass, large Visible Precipitate in the bottom and a precipitate on the air pipe.

In this test it was observed that the heat-treated mixtures (24 hours) presented, after the test (15 days later) an evolution or "Maturation", which consisted of the following: In the treatment No. 1 the product passes from "Slight Haze" to "Slight Haze and Slight Precipitate". Treatment No. 2 did change from "No Haze" to "Intense Haze passing the filter and slight precipitate. The treatment 3 did change from "Slight Haze and visible precipitate" to "No Haze and large more visible precipitate. Likewise treatment No. 4

After 15 days of the heat treatment, the insoluble were filtered under pressure in a fast qualitative filter paper 68 mm in diameter. Most insoluble were found strongly adhered to the glass. They were flushed with Varsol (White Spirit) both the filter and the container. All samples filtered easily. It is noteworthy that the sample No. 2 with Intense Haze, completely passed through the filter with no apparent decrease in its Haze. This is an indication that the precipitation of gum in this sample besides being produced in smaller amounts, their production was slower than in the other treatments. His Haze was formed during the subsequent "maturation" after the heat treatment. Besides that, its particle size was extremely fine, almost colloidal, and filtered easily trough the filter paper used. Under these conditions it was not possible to quantify the amount of colloidal gum formed.

After the filtration and washing with Varsol, it proceeded, without drying, to the dissolution of the gum precipitated in both the container and filter using Thinner, collecting the filtrates in respective beakers. All adherent gums were dissolved easily in the Thinner and passed without any difficulty trough the filter.

Gums dissolved in Thinner, were dried at the atmosphere in glass crystallizers for 24 hours during which evaporated approximately 70% of the liquid phase, then they were transferred to Petri dishes and placed on hot surface at 60 ° C, for 24 hours and finally introduced in drying oven at 70 ° C for 60 hours.

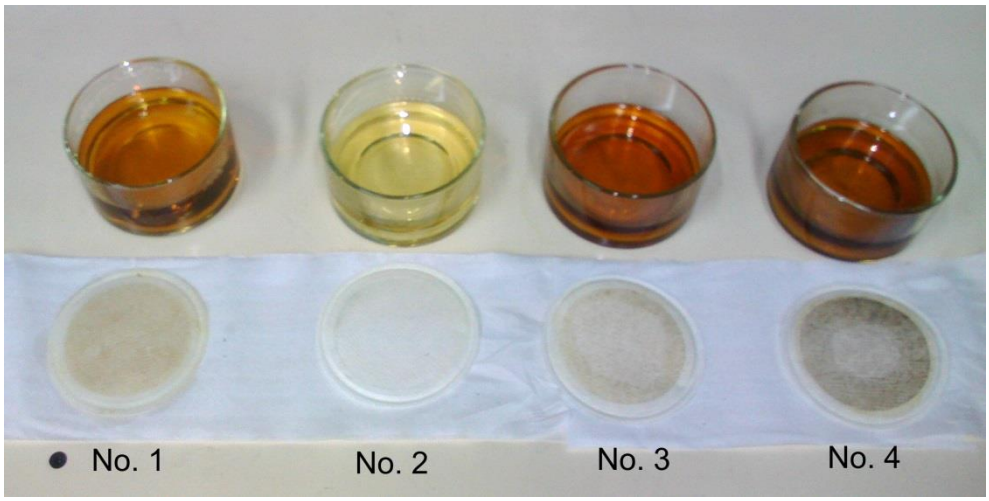


Fig. 4. Appearance of the filters and crystallizers before drying.

The presence of insoluble gums was observed which remained on the filter paper, even after washing with Thinner. Its mass, apparently, was well below the weight of the soluble gums obtained. A greater proportion were present in treatment No. 3 and No. 4, milder in the No. 1 and almost unnoticeable in the # 2

Fig. 5 Appearance of the filters after drying and the gums in petri dishes before final drying.

The results of this experiment are shown in the following chart:

	Productos:			
Combustible Utilizado en todas las muestras: Mezcla 50/50 v/v				
	Aditivos	Ref.	Dosis	
			uL/L	mg/lt
1	Orco	DKC-3468-XCH	1000	100.6
2	Simoniz	Qualitor	3120	46.6
3	ACPMax		2462	262.6
4	Testigo Absoluto		0	314

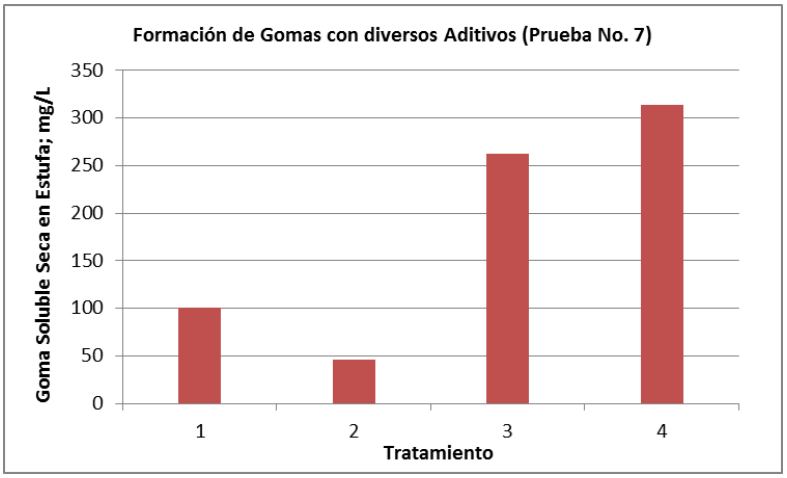


Fig. 7. Influence of the additives on Gum Formation in the mixture 50/50 of Diesel Terpel and Diesel DPC.

Most gums (Fig. 8.) corresponded to Soluble Gum (in Thinner), however, a small amount, unquantified in this experiment was produced as additional insoluble gum which remained attached to the filter, as can be seen in picture No. 5

Fig. 8. Oven Dried Gum at 70°C for 60 hours.

CONCLUSIONS

The effect of the additives used in the mixture 50/50% v/v of the diesel fuel derived from plastic with conventional Diesel fuel B10, as to the formation of gums is remarkable both in quantity and time, speed of formation, the particle size and the tendency to agglomerate thereof. Product # 2 substantially lowers the amount of formed gum, delays the formation rate, decreases particle size

and decreases the agglomeration tendency thereof in the final product. Product No. 3 had little effect on the formation of Gums. Product No. 1 had good effect, although lower than No. 2.

It is recommended to test the product No. 1 in higher dose than that used in this experiment, since, in the absence of economic considerations, this product is at a disadvantage because the product dose versus # 2.

References

Westbrook, S. (2005). *An Evaluation and Comparison of Test Methods to Measure the Oxidation Stability of Neat Biodiesel.* National Renewable Energy Laboratory -NREL- Southwest Research Institute. San Antonio -Texas-: National Renewable Energy Laboratory -NREL- Southwest Research Institute.