FORMATION OF GUM IN MIXTURES OF PLASTIC DIESEL WITH DIESEL B10

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ABSTRACT:

The results of Gum formation in mixtures of Diesel derived from plastic, DPC, with conventional Diesel Terpel B10 are reported in this paper.

Keywords:

Plastic Diesel, Gum Formation, Oxidation Satbility.

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 match 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, this process does not guarantee the quality of the fuels produced 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 re-polymerization and Gum formation.

This, coupled with the presence of oxygen in the products, which is introduced into the process as a contaminant from biomass, food waste and paper present in processed wraps, increases the instability of fuel and the tendency to gum formation, resulting in soiling valves in gasoline engines and obstruction of filters and injection systems in 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 this engines use the fuel. In carburetor engines, the gasoline is injected first into the intake manifold and from there it goes to the cylinder. So, if there are any nonvolatile gums present in the fuel, they will tend to accumulate in the intake manifold as well as in the admission valves. While in diesel engines, the fuel is directly injected into the cylinder or in some cases to pre-combustion chambers, process in which, the formation of gum is less problematic than in the case of gasoline engines where it is injected in the manifold before the valves.

In order to contribute to the solution of this problem, it has been evaluated gum formation (Susceptibility to oxidation) of the diesel derived from the pyrolysis of plastics waste mixed with conventional diesel fuel (B10) in Colombia, more specifically in the City of Bogotá DC

2. MATERIALS AND METHODS

2.1. Plastic Derived Fuel –DPC-

The Diesel fuel derived from plastic, hereinafter called Plasticombustible or Diesel (DPC), 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 distilled between June and September/2015 and 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 as obtained in June 2015

ANÁLISIS DE COMBUSTIBLES

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

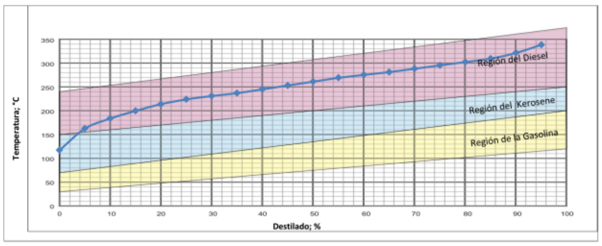
Curva de Destilación ASTM D 86

	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. ASTM D86 distillation curve for Diesel DPC, at atmospheric pressure in Bogotá, 560 mm Hg.

2.2. 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

2.3. Equipment for measuring Oxidation Stability.

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

	ASTM 2274	This Test
Temperature of the Test; °C	95	90
Testing Time; hr	16	24
Size of Testing Sample; ml	350	500
Circulating Gas;	Oxygen	Air
Gas Flow; lt/hr	3	60
Condenser and Gas Injection tube material;	Glass	St. Steel 304
Filter Drying Temperature; °C	80	70
Filter Drying Time; hr	0.5	24
Solvent for washing insolubles:	IsoOctano	Varsol
Solvent for Soluble Gum:	Trisolvente	Tinner

Where

Trisolvent , a mixture of equal volumes of acetone, methanol, and toluene.

And Tinner is a commercial solvent mixture, according to Wikipedia composed of:

Tinner	
Sustancia	**Porcentaje**
Tolueno	5–50%
Alcohol metílico	15–50%
Cetonas	5–40%
Hexano	5–30%
Xileno	5–20%
Ésteres	3–50%

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

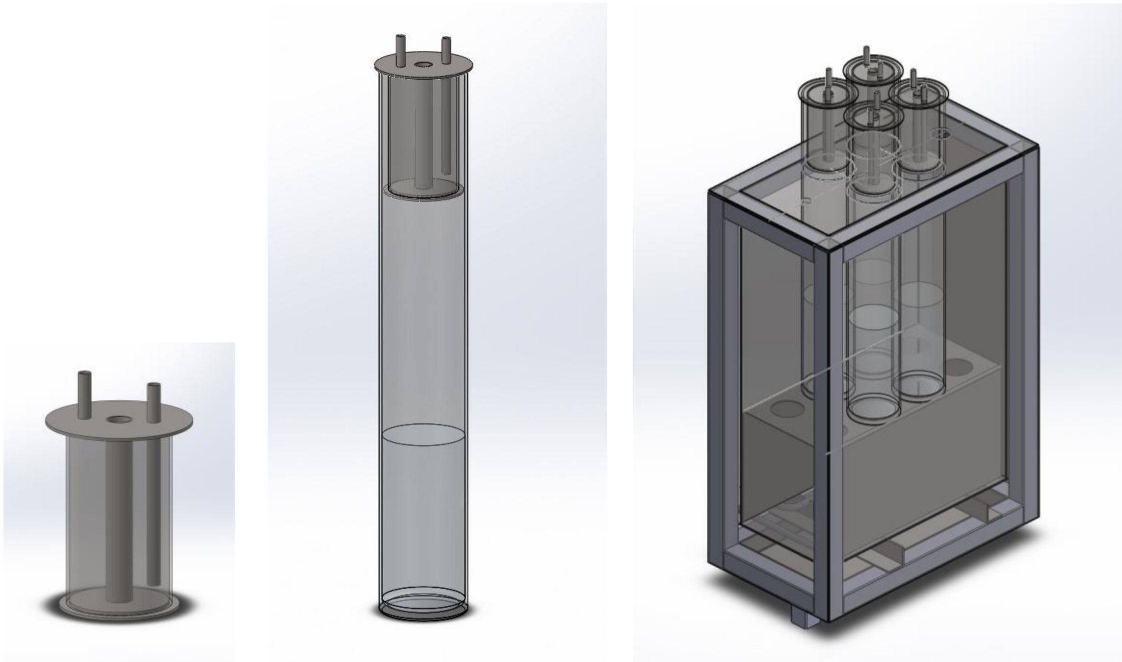


Fig.2. Equipment used in this test; a) Condenser Stainless Steel 304; b) glass tube and condenser; c) thermal bath with 4 tubes.

Fig.3. Equipment as seen during the test.

2.4. Tested Mixtures.

The mixtures used in this test (Test No. 3) were conducted by volume with the following proportions:

1. Diesel Terpel B-10 - 100 % : Diesel DPC – 0 %
2. Diesel Terpel B-10 - 50 % : Diesel DPC - 50 %
3. Diesel Terpel B-10 - 75 % : Diesel DPC - 25 %
4. Diesel Terpel B-10 - 0 % : Diesel DPC - 100 %

Fig.4. Mixtures image before the test

3. RESULTS AND DISCUSSION

The test was running normally and at the end thereof, the tested mixtures were slightly more turbid than at the beginning thereof. In Mixture # 4 adherent gum ring on top of the liquid was observed. Similarly in the # 2 and 3 mixtures, the ring was almost invisible.
In the air injection tubes, the adherent gum ring was also observed, with greater intensity in the mixture No. 4 (DPC 100%), almost imperceptible in Mixture No. 2 (DPC 50%) and not noticeable in mixture # 3 and # 1 (DPC 25% and 0%).

Fig.5. Picture of the tubes for Air Injection.

The insoluble material was filtered at atmospheric pressure in a qualitative filter paper, 20 cm diameter, and then it was flushed with Varsol (white spirit) both the filter and the container and the air injection tube of the test. There was a strong tendency to clogging of the filter, especially from the gum in sample Diesel DPC-100%, which was so slow to filter that it took more than two days. After filtration, washing with Varsol and dried the filter, we proceeded to lavage (dissolution) of the gums present in both the container and filter, using Thinner and collecting the filtrates in respective beakers.

Fig.6. Mixtures image after the test. Note adherent Gum ring on top of Mixture No. 4

Gums dissolved in Thinner, were dried into the atmosphere in Petri dishes and then introduced into drying oven at 70 ° C for 24 hours.

The presence of insoluble products were observed, which remained on the filter paper, even after washing with Thinner.

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

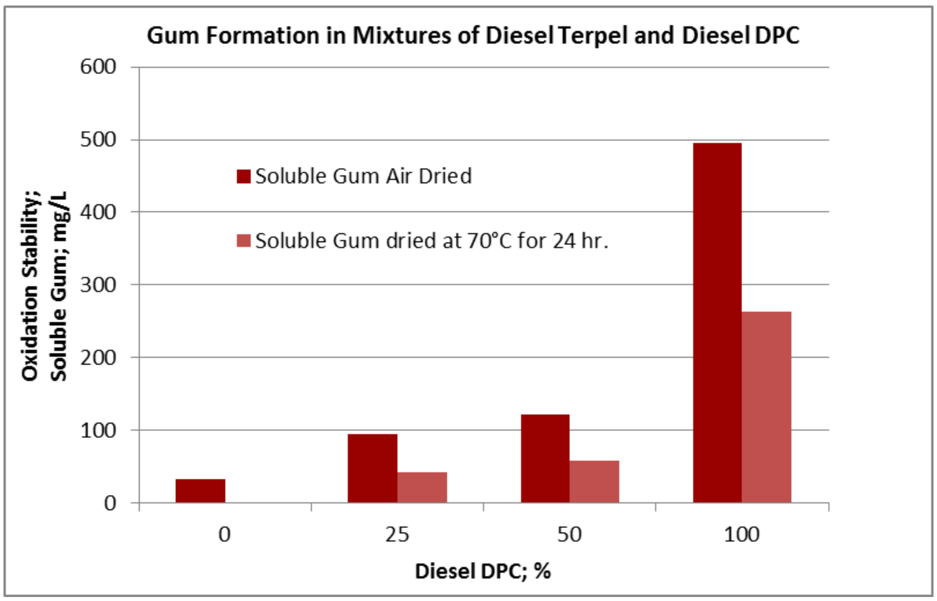


Fig.7. Gum formation in mixtures of Terpel Diesel and Diesel DPC.

	Sample		GSSA; mg/L	GSSE; mg/L
1	Diesel Terpel 100 - DPC 0	0	33	0.00
3	Diesel Terpel 75 - DPC 25	25	94.8	42.4
2	Diesel Terpel 50 - DPC 50	50	121.2	57.4
4	Diesel Terpel 0 - DPC 100	100	495.8	263.60
	MSA	Air Dred Sample		
	MSE	Oven Dried Sample; 70°C x 24 hr		
	RSA	Air Dried Residue		
	RSE	Oven Dried Residue; 70 °C x 24 hr		
	GSSA	Soluble Gum, Air Dried		
	GSSE	Soluble Gum, Air Dried; 70 °C x 24 hr		

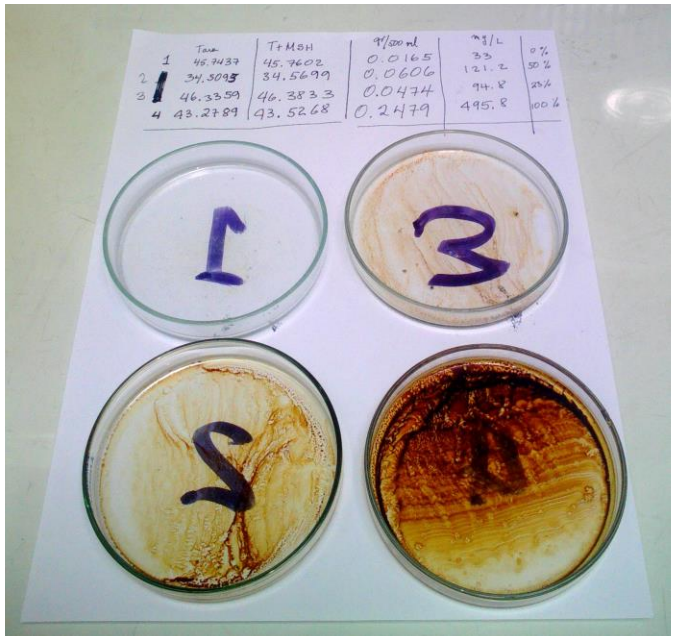


Fig.8. Soluble Gum, Air dried GSSA.

Most gum 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.

Fig. 9. Insoluble Gum formation in mixtures of Diesel Terpel and Diesel DPC.

CONCLUSIONS

The Diesel fuel mixture composed of conventional Diesel B10, and the plastic derived diesel DPC, substantially lowers the gum formation in the final product, being its effect greater than the proportion used in the mix.

The DPC 25% mixture allows to obtain a Diesel Fuel with a gum forming (oxidation stability) of 42.4 mg/L in 24 hours (Equivalent to 28.3 mg/L in 16 hours). It is noteworthy that the Decree 90963 of the Ministry of Mines and Energy of Colombia establishes as a ceiling for test ASTM D-2274 a value of 25 mg / L in 16 hours.

This suggests that up to 20% of DPC Diesel mixed with 80% of Diesel B10 would be a product that could pass the ASTM D 2274 standard.

The decrease in gum formation, rather than being proportional to the amount of Diesel B10 used in the mixtures may represent the inhibition of polymer formation caused by the biodiesel, present in the Diesel B10, as suggested in NREL/SR-540 report 38 983, page 20 (Westbrook, 2005).

It is suggested that this trial should be continued as well as assaying some antioxidants mentioned by Westbrook (Westbrook, 2005) such as BHT and TBHQ and one anti-polymerizing agent suggested by the author based in Hydroquinone.

Bibliografía

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.