HEAVY HYDROCARBON-COAL SURFACTANT-WATER-CCTA MIXTURE TECHNOLOGY. SEMI-INDUSTRIAL EVALUATION

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Using low viscosity inverse emulsion (o/w) technology of fuel oil in water, developed at the Instituto Colombiano del Petróleo, ICP, a synergy with the Coal-Surfactant-Water (CCTA) systems was established, yielding a new fuel mixture called CCTA, Coal-Fuel Oil-Surfactant-Water. This triple system holds microscopic droplets of fuel oil and solid coal powder particles (up to 30% in weight) in suspension, in a water continuum medium. In the study performed, the stability during storage and pipeline transport at a semi-industrial scale of the CCTA systems was evaluated at two temperature ranges. The results show stability of over 30 days under testing conditions. In the ICP fuel evaluation unit, several different nozzles of comercial use with liquid fuels and different ratios of excess oxygen were evaluated finding some conditions appropriate for the burning of this non-conventional fuel. Likewise, the monitoring of emissions during the combustion process was performed, observing low contaminant levels in comparison with other liquid fuels.

Utilizando la tecnología de emulsiones inversas (o/w) de baja viscosidad de combustóleo en agua, desarrollada en el Instituto Colombiano del Petróleo (ICP), se estableció una sinergia con los sistemas de Carbón-Tensoactivo-Agua (CCTA), para dar como resultado una nueva mezcla combustible denominada CCTA, Carbón-Combustóleo-Tensoactivo-Agua. Este sistema triple, tiene en suspensión gotas microscópicas de combustóleo y partículas sólidas de carbón pulverizado (hasta el 30% en peso), en un medio continuo constituido por agua. En el estudio realizado se evaluó la estabilidad en almacenamiento y transporte por tuberías a escala semi-industrial de los sistemas CCTA a dos rangos de temperatura. Los resultados obtenidos demuestran que la estabilidad supera los 30 días bajo las condiciones de prueba. En la unidad de evaluación de combustibles del ICP se evaluaron diferentes boquillas de uso comercial con combustibles líquidos y diferentes relaciones de exceso de oxígeno, hallando unas condiciones apropiadas para la quema de este combustible no convencional. Igualmente se realizó el monitoreo de emisiones durante el proceso de combustión observándose niveles de contaminates bajos en comparación con otros combustibles líquidos.

Keywords: *coal, fluid mixtures, non-conventional fuel, combustion, emissions.*

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INTRODUCTION

This study arises from the need to develop alternative ways to extend and increase the use of coal as an energy resource; the research was carried out during Phase II of the project of Emulsion Preparation, Transport and Combustion of Emulsions and Dispersion of Heavy Hydrocarbon and Powdered Coal, partly financed by Ecocarbon and Colciencias. A triple system called CCTA, of low viscosity, transportable through pipelines, stable to sedimentation, was obtained during the first phase, at a laboratory level, and a small pilot (Ecopetrol - ICP, 1996), with promising combustion results as observed in the preliminary tests.

The objective of this second phase was the optimization of the conditions for preparation, transport, combustion and the monitoring of emissions of the CCTA triple system continuosly at a semi-industrial pilot scaled facility.

It is important to mention that there is no report with this kind of fuel mixtures, particularly with the concentration, type of solids used in the formulation and also with the low viscosity exhibited by the CCTA mixture.

MATERIALS AND METHODS

An appropriate formula was selected in regard to the concentration of additives, the coal particle size distribution, etc., to obtain a CCTA mixture with a coal content between 20% and 30%, using the thermal export type coal called Granzon, a fuel oil of 0.636 kg/ms (300 SSF), as the raw material, and a dispersing and emulsifying additive agent developed at the ICP. The characteristics of the coal, as well as the fuel oil, are shown in Tables 1 and 2, respectively.

Pipeline production preparation.

Based on prior studies (Suárez, 1994; Leal, 1995) and those performed in parallel in the laboratory, a series of facilities to obtain the CCTA mixture was designed and built, with the support of static mixers according to the ICP design, previously selected in phase I of the research.

In the chart shown in Figure 1, the schematics of the facility to obtain CCTA, with the capacity to prepare up to 1,000 kg/h can be observed.

Table 1. Granzon carbon properties

Property	
Heating power (MJoule/kg)	31.33
Volatile matter (weigh %)	36
Ashes (weigh %)	7.3
Residual humidity (weigh %)	1.73
Sulfur (weigh %)	0.72
Swelling 0.636 kg/ms index, FSI	2.5

Table 2. 300 SSF Fuel oil properties

Property	
Viscosity (Pa)	
323 (K)	0.988
308 (K)	4.239
298 (K)	12.210
Heating value (MJoules/kg)	41.75
Sulfur (weigh %)	1.298
Vanadium (kg/m^3)	0.250
Nickel (kg/m^3)	0.121
Sodium (kg/m^3)	0.080

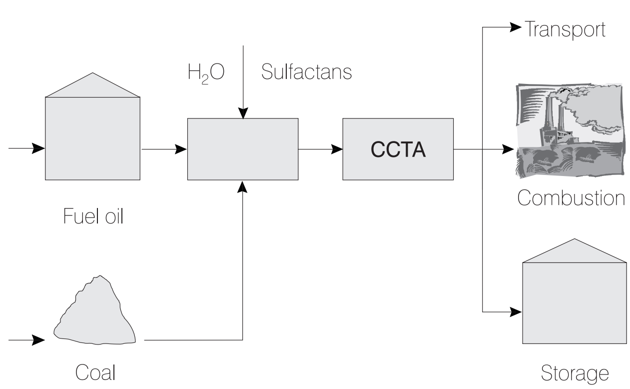

Figure 1. CCTA preparation process

The CCTA mixture obtained at the facility was used for the evaluation of the pipeline transport, stability to sedimentation, but basically for the combustion process.

Evaluation of pipeline transport

This evaluation was carried out in the loop of dynamic fluid tests, MCPFD, of the ICP (Grosso *et al*, 1996), in which, once the mixture was characterized in regard to viscosity and particle size distribution, it was pumped through 1/2 and 1 inch internal diameter tubing, maintaining a temperature at 293 K and 303 K, automatically registering the system's pressure drops through a distributed control system I/A, FOXBORO, WP-30.

Evaluation of storage and static stability

In order to simulate the most critical storage condition to which a CCTA mixture could be subjected, 1.11 m^3 (7 barrels) capacity tanks were modified with coils for heating and cooling in which the CCTA triple system was stored without any type of agitation and at two temperatures, 293 K and 313 K.

Each tank was subjected to a strict follow up and control of temperature and CCTA properties against time. The properties evaluated were viscosity, particle size and coal percentage taken at three points; top, middle and bottom of the tank.

Evaluation of combustion

For this evaluation, the ICP's Combustion Evaluation Unit was used, with a design capacity of 5,275.2 MJoule/h (5 Million BTU/h) and versatile system for the supply of fuel and steam or air for atomization. The chamber's burner allows easy and quick exchange of different nozzle configurations, as well as the thermic profile measurements, SO_2, NO_x type emissions, particle material, CO_2, CO, opacity, excess oxygen.

This unit operated with the CCTA prepared at the facility, changing the operating conditions relative to the fuel's atomization (spray), atomizing medium, air excess, type and nozzle configurations.

All the nozzles used in the tests were "Peabody" type, which is schematically represented in Figure 2. Here, the atomization medium flows through the center while the fuel flows through the annulus, producing the mixture of fuel and atomizing medium at the exit of the annular section which is then atomized through the tip's holes. Commonly, this type of nozzle "plug" has from three to eight holes on the rings and six on the "tip".

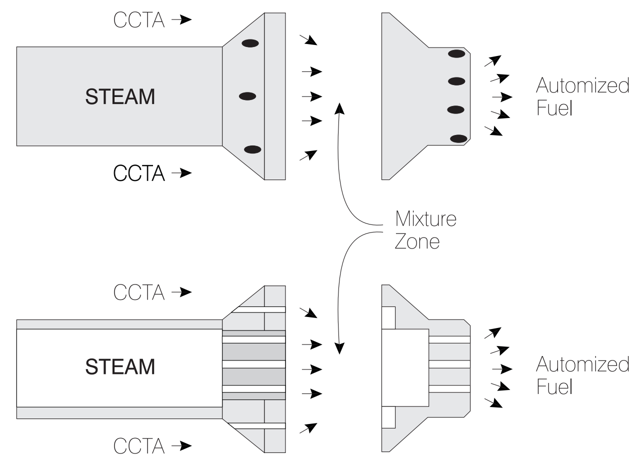

Figure 2. Type of nozzle configuration used in the combustion test.

In all the evaluations carried out, the CCTA characterization was performed with the following equipment: Viscosimeter of coaxial cylinders Haake model, Malvern droplet and particle sizer series 2600c and a Parr heatmeter pump.

RESULTS AND DISCUSSION

Characterization of the raw materials

Besides the properties shown in Tables 1 and 2, a detailed characterization of the coal particle size for the preparation of CCTA was carried out. Likewise, a fuel oil rheology study was performed and compared with the inverse emulsion (o/w), ECA, obtained from it and its CCTA triple mixture, where the coal contents varied from 20% and 30% in weight.

As shown in Figure 3a, the distribution of the Granzon coal particle size is of the bimodal type, and unlike previous studies (Suárez, 1994; Leal, 1995), there is a high percentage of particles above $74 \cdot 10^{-6}$ m (74 microns) or mesh 200. The coal's bi-modal character grants low viscosity special properties to those fluid systems that have been prepared with it.

The viscosities of the 0.636 kg/ms (300 SSF) fuel oil and 30% coal CCTA inverse emulsions are of the same magnitude and almost 100 times less than the viscosity of fuel oil at 298 K, as shown in Figure 3b.

Evaluation of the pipeline transport

Figures 4a and 4b show data from the CCTA mixture transport simulation, in comparison with the fuel

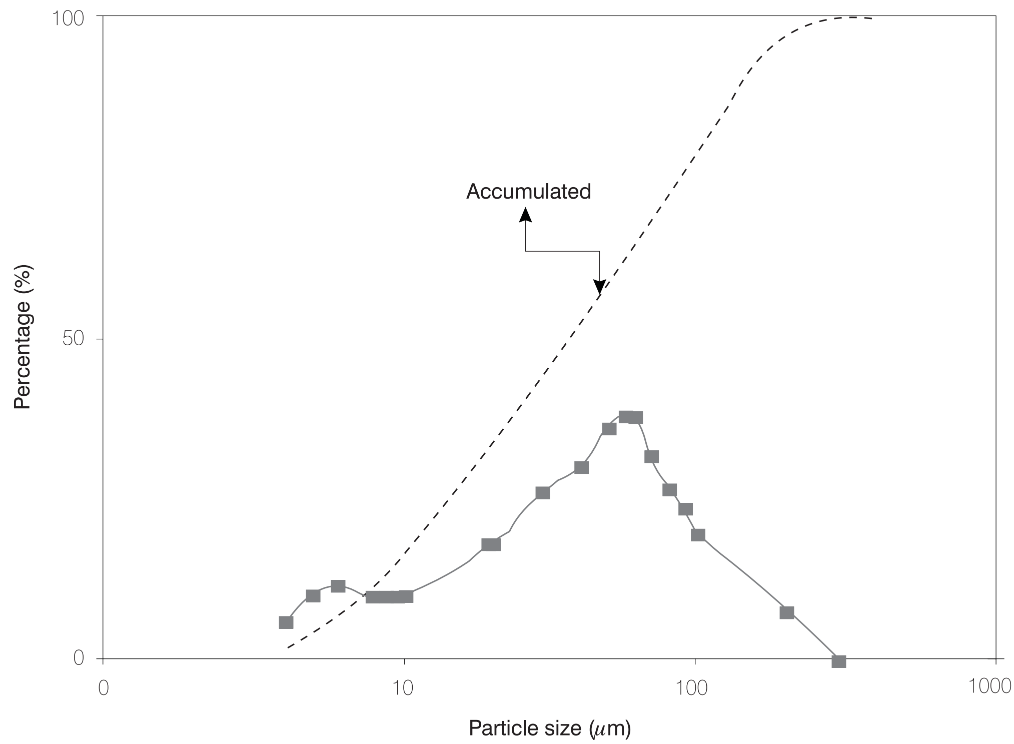

Figure 3a. Particle size distribution of Granzon coal

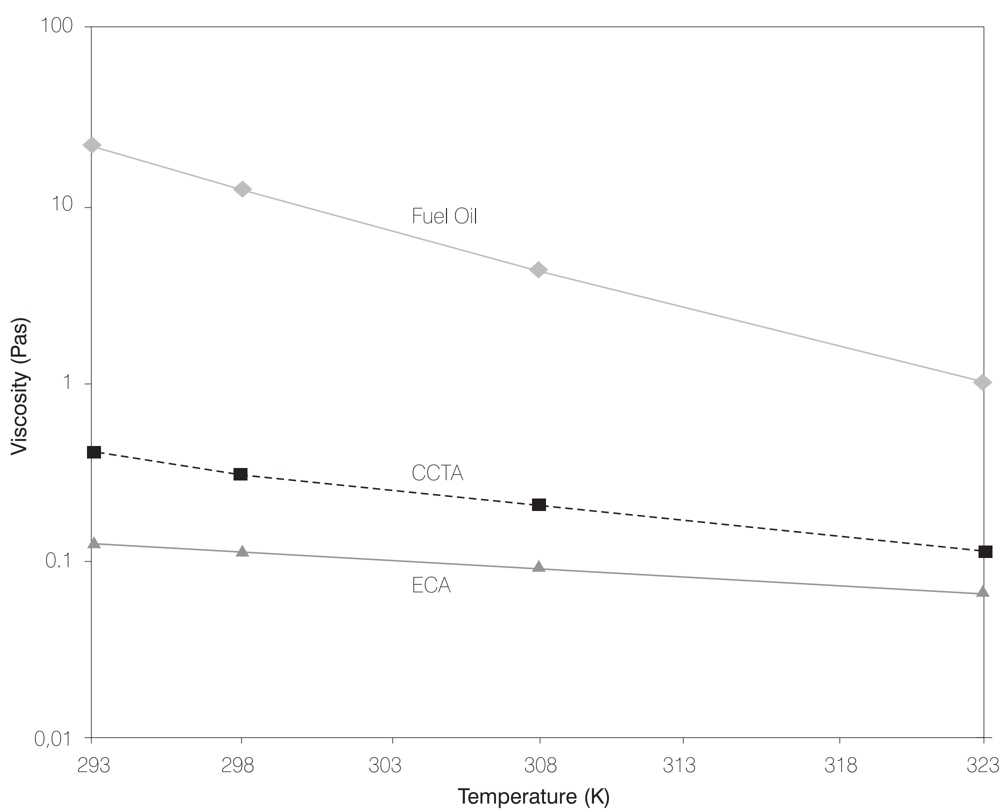

Figure 3b. Viscosity curve of fuels evaluated

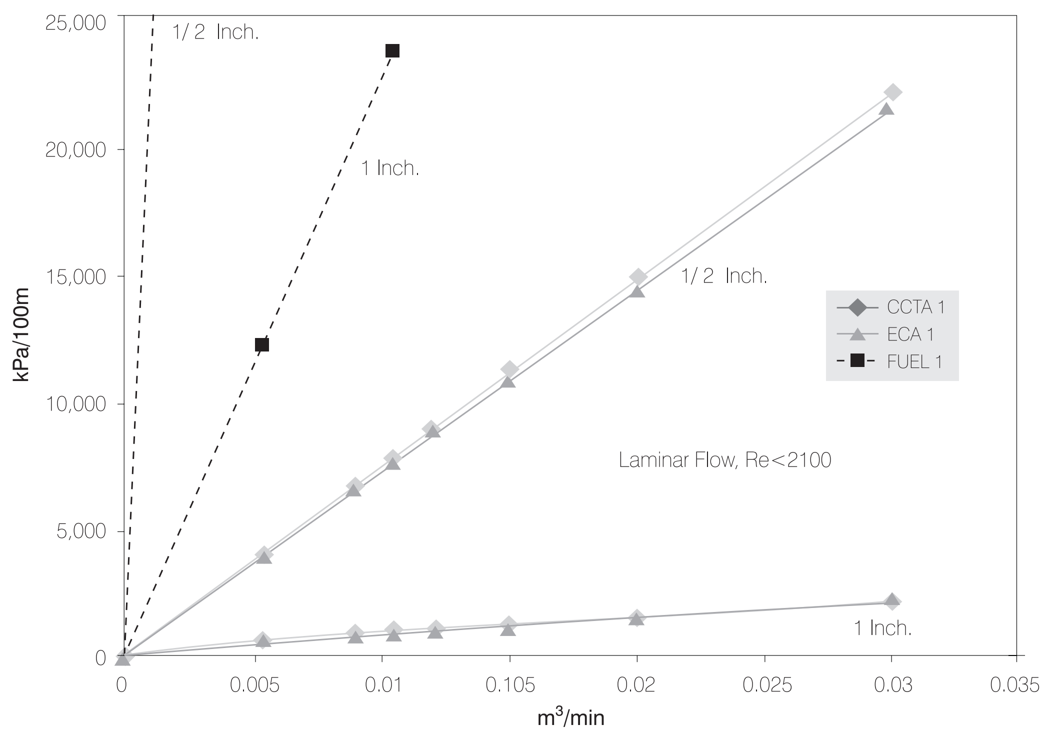

Figure 4a. Pipeline transport simulation for the CCTA mixture, 303 K

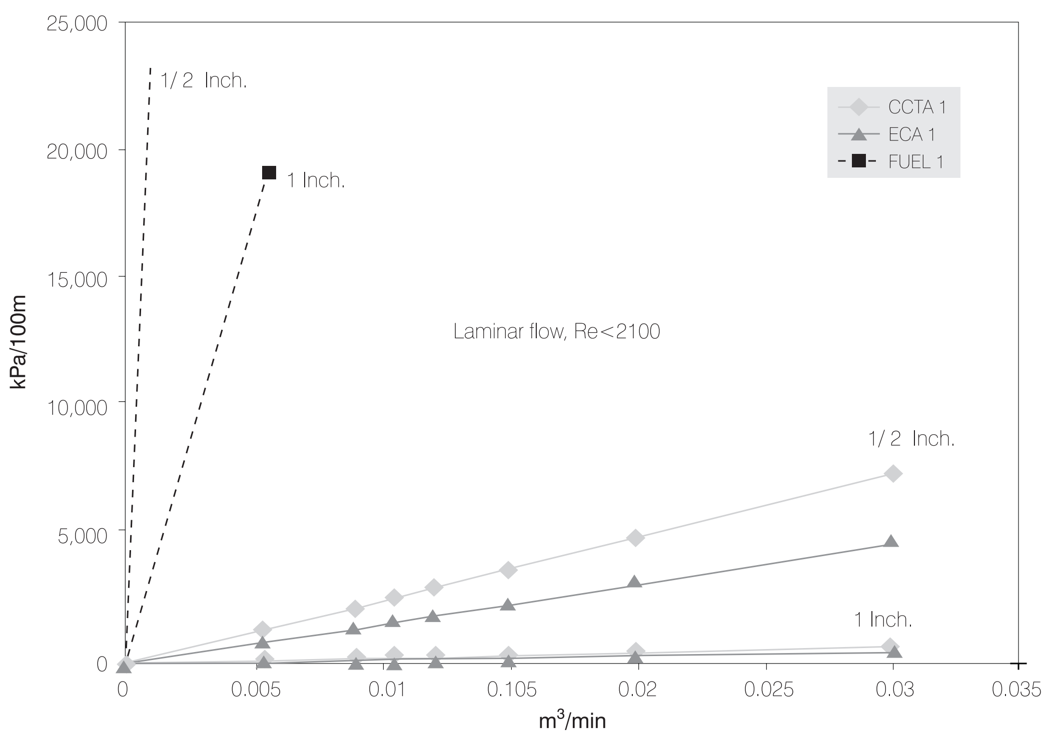

Figure 4b. CCTA mixture, pipeline transport simulation, 293 K

oil inverse emulsion and the fuel oil. Measurements were taken at two temperatures ranges, 293 K and 303 K and within a laminar flow, observing that at 303 K the pressure drops of the CCTA systems with 30% coal and the inverse emulsion o/w were very similar. As proven in phase I (Ecopetrol - ICP, 1996), the fluid mechanics equations are applicable to the CCTA mixture case, without requiring complicated or complex mathematical models (Turian and Yuan, 1977; Aude *et al*, 1971).

Some differences in the pressure drops between the CCTA and the emulsion (ECA) can be observed at 293 K, fact that can be explained by the existence of greater sensibility of the viscosity with the temperature reduction for the CCTA than for the ECA, but despite these differences, the low pressure drops generated make these systems easily transportable through pipelines.

Evaluation of storage and static stability

The behavior of the variables analyzed during the test: viscosity, coal particle size and percentage, measured at three depths from each tank, present the tendency shown in Figure 5, in which the stability results at storage without agitation are shown, such as the variation in time of the CCTA mixture particle size.

Considering the test design is the worst of storage conditions for a fluid with a solid in suspension, the results shown in Figure 5 where it is affirmed that the CCTA triple system is stable during sedimentation under these conditions, as since can be seen in the Figure, the variation in the monitored properties at the three depths are minimal after the first five days of storage, situation that can be operationally remedied with an agitation system, mechanical or re-circulating, with a pump at low flow.

Evaluation of combustion

This evaluation was divided into two parts. In the first part, operational conditions and the handling of the new CCTA fuel were determined, and in the second, the emissions were monitored with combustion process stable conditions.

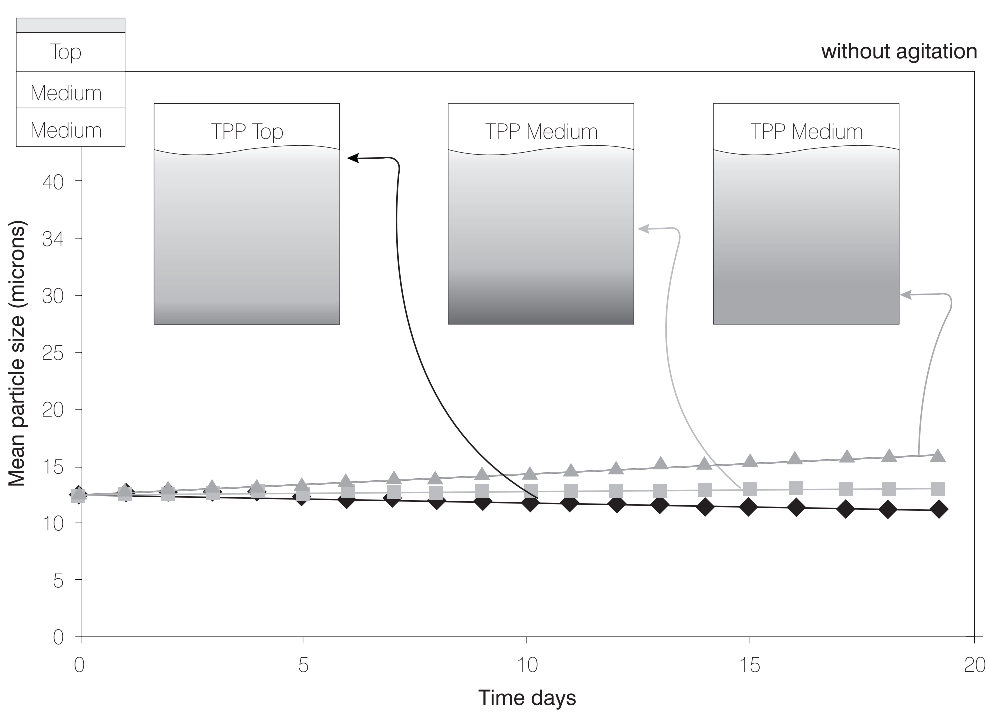

Figure 5. Storage stabillity evaluation for the CCTA, 313 K

In the first stage combustions were performed for 30 days, using steam and air as the atomizing medium. The work was carried out with excess oxygen percentages from 1% to 4%, using different nozzle configurations used commercially in liquid combustion.

The preliminary tests allowed the following specifications:

- To work the fuel evaluation unit at a thermal charge of about 60% of the design capacity (5,275.2 MJoule/h), to protect the refractory because of the heat storage due to the hours of daily activity and to the system's lack of refrigeration.
- The atomization with steam worked better than with air. Once the appropriate flow of atomization steam was controlled, the steam's temperature controlled the viscosity at the nozzle point, keeping all the holes unclogged. The control was kept at a ratio of 0.30 kg steam/kg fuel, a low ratio being that the water content in the fuel helps in the atomization process.
- Fuel's room temperature. The average CCTA temperature during storage and in line until reaching the burner was 299 K.
- The PEABODY type nozzle was selected, modifying its design for this application.
- Percentages of residual oxygen in vent gases, lower than 3% vol.

Keeping the previous conditions fixed, the variables are: furnace temperature, which increases with the test time period, due to the lack of refrigeration and the residual oxygen percentage in the fuel products. This is useful to recognize the influence of these two variables on emissions and flame behavior.

All the monitoring of the atmospheric emissions was performed through the available in line equipment and sensors in the Combustion Chamber. The following emissions were quantified:

- Sulfur Oxides (SO_2)
- Nitrogen Dioxide (NO_2)
- Coal Monoxide and Dioxide (CO and CO_2)
- Opacity and Particulate Material. For the latter, the EPA standard of determining Material emission in fixed sources was applied (Method 5).

The results are compared with the Current National Standards (Decree 02) and the US Standards.

All the operation variables were continuously monitored and the general average calculations were performed, taking into consideration the thermal capacities achieved. During the operation, the fuel, the operating conditions and the equipment involved were continuously controlled to maintain the chamber stable, thus guaranteeing a good monitoring of the emissions.

The obtained results are compared with data from experiences with 2.12 kg/ms (1,000 SSF) Fuel oil at 323 K. This will give a better idea of the type of benefits that can be expected.

Flame luminosity. Qualitatively, the flame luminosity towards the back of the nozzle is lower during the CCTA combustion compared with that from the fuel oil. However, it remains within the detection range of the flame intensity sensor tool.

The atmosphere within the chamber looks slightly opaque due to the effect of the coal's ashes and the water contained, in contrast to fuel oil consumption where it looks much clearer. The color of the flame, in both cases, is a clear bright yellow. During the tank change, a small amount of sparks is present, caused by larger than average coal particles. This is very noticeable in the chamber because of its narrow size. In industrial equipment, the atomization steam can be adjusted during the tank change period, in order to prevent this behavior.

Efficiency. There is no heat recovery in the combustion chamber, therefore is not possible to determine the thermic efficiency of the equipment as in the case of a boiler. However, according to experiences with ECA, we can expect the compared efficiencies between the CCTA and the fuel oil, to be similar. The effect of the greater amount of ash generated by the coal, is reduced by cleaning the pipes with "SOFTBLOWER" steam injection.

It is known that approximately 2.8% of the gross heat generated by an emulsion of this type, is consumed when evaporating the water contained in the fuel. This energy is recovered inside the boiler by the greater amount of heat generated as a result of greater combustion efficiency (lesser residual CO and unburnt products), greater efficiency in heat recovery by cleaner transferring surfaces and by the loss reduction in the combustion gases due to minor requirements for air and steam atomization. This is verified during the industrial test.

Noise level. The noise produced by the burner and the fan was not monitored for this evaluation, since the result in an industrial situation can not be scaled. This is determined during the industrial test.

Table 3 shows the operation parameters selected to achieve a good combustion in the chamber with the selected nozzle.

Monitoring of atmospheric emissions

A monitoring of the atmospheric polluting emissions was performed during the CCTA's consumption period. Most of the available sensors were placed on line and the Particulate Material was periodically measured with the equipment of Method 5, according to the EPA standards.

In Colombia there are no specific standards for special fuels such as the emulsion, therefore, comparison was carried out under US EPA Standards. In the country, the sulfur content is limited to 1.7% in weight, which the CCTA meets, however it does not meet the EPA standard in regards to SO_2 emissions that according to the Standard is 344.04 kg/MJoules (0.8 lb/MMBTU), the CCTA obtained a value of 662.27 kg/MJoules (1.54 b/MMBTU), thus the need to perform the emission control.

Likewise for the Particulate Material, the EPA Standard is 43 kg/MJoule (0.1 lb./MMBTU) and the CCTA emission is 1,010.61 kg/MJoule (2.35 lb/MMBTU) without the use of electrostatic precipitators.

The EPA Standard is met in regards to the NO_x emission which is 129.01 kg/MJoule (0.3 lb/MMBTU), the average value for the CCTA was 73 kg/MJoule (0.1 lb/MMBTU).

The NO_x emission increases when the atomization differential is increased, producing a greater amount of steam, and hence increasing the temperature of the flame and the fuel mixture in the furnace room, a thermic condition that promotes the oxidation of the nitrogen present in the air.

Figure 6 shows a comparison of the CCTA emissions with other fuels including Fuel oil, Castilla crude oil, fuel in water emulsion (ECA), and of which a similar study was performed at the ICP combustion evaluation unit and at Barrancabermeja's Industrial Complex. Data for the Orimulsion were taken from the Internet at hhtp: //Our World.compuserve.com/ homepages/orimulsion/ enu-fact.htm.

This Figure shows that the emissions from the particulate material are very high in comparison with those from other liquid fuels, it must be noted that this

Table 3. Comparison of the operation variables of the CCTA with other fuel oils.

Variable	CCTA	Castilla	Fuel oil
Flow velocity (m^3/min)*100	1.9682	1.4761	1.2112
Generated energy (MJoule/h)	3,270.62	3,692.64	3,270.62
Furnace room temperature (K)	1,573 - 1,623	1,573 - 1,723	1,523 - 1,623
Residual oxygen (%)	1 - 2.0	2.0	3.5
Atom. steam (kg steam/kg comb)	0.3	0.35	0.48
Atom. differential (kPa)	172.37	68.95	103.42
pineline fuel temperature (K)	299	333	358
Burner fuel temperature	299	373	393
Flame length (m)	0.91 a 1.52	0.91 a 1.52	0.91 a 1.52
Vapor pressure in burner (kPa)	496.42	675.68	703.26
Comb. vapor pressure in burner (kPa)	324.05	606.73	599.84
Duty (% of total capacity)	60	70	60
Nozzle	Peabody	Peabody	Peabody

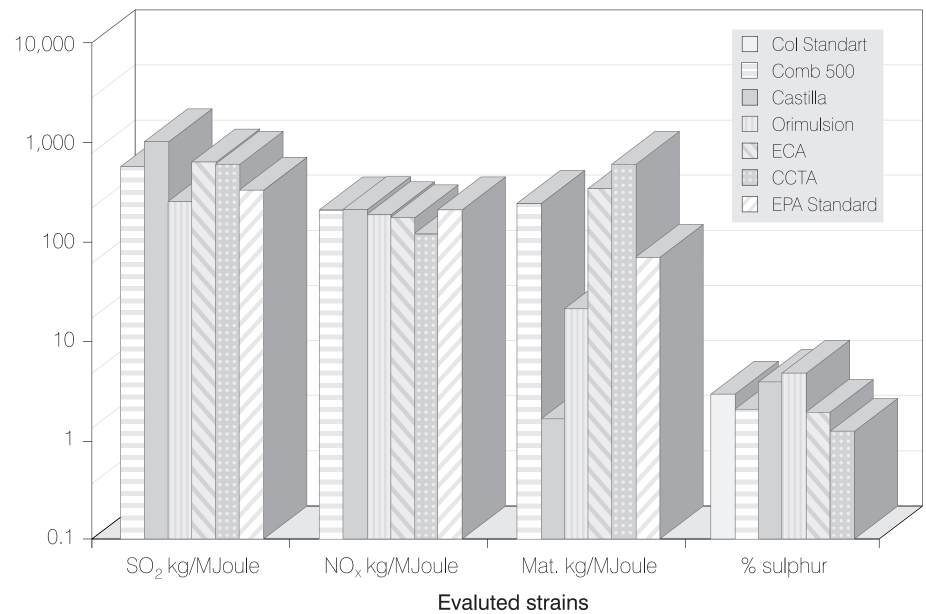

Figure 6. Comparison of CCTA emissions with other conventional and non conventional fuels. Orimulsion data were taken from the web site: http://ourworld.compuserve.com/homepages/orimulsion/enu-fact.htm

result was obtained before utilizing the treatment with an electrostatic separator. Normally, the efficiency of the electrostatic separators is greater than 90%, which would allow a reduction in the CCTA emissions to values less than 86.01 kg/MJoule (0.2 lb/MMBTU).

Table 4 shows the operations conditions obtained for the CCTA at 60% and 65% of the combustion chamber thermic capacity, as well as the averages and ranges obtained in operation for the most important variables.

CONCLUSIONS

- This study allowed the gathering of a great amount of technical and operational information, that will be fundamental for establishing criteria for a future industrial scale-up. It also gave more solid basis for a technical-economic study directed towards the industrial application of the technology, a basic aspect for the marketing of the CCTA.
- The CCTA triple system technology contributes to the improvement of the coal combustion processes, easing its handling in liquid form, with greater thermic efficiency and lesser unburned residual generation, in comparison with solid coal combustion.
- The CCTA technology is applicable on a wide variety of coals, with only slight adjustments in the formulas, since this evaluation was developed with a type of coal different to the one used in phase 1 and in the works of Suárez (1994) and Leal (1995).
- The MCPFD fluid-dynamic studies showed that the CCTA mixtures have behavior similar to the inverse emulsions o/w, fuel oil/water, showing sharp pressure drops when transported through pipelines.
- At low flow and low laminar flow, the CCTA mixture showed easy transport and stability. The fluid-dynamic results easily adjust to the fluid transport fundamental equations and are in agreement with the viscosity results obtained in the laboratory.
- The CCTA stored without agitation, remained stable for the 30 day-test-period at the two temperatures evaluated, 293 K and 313 K, despite the critical condition in which the test was conducted.
- About 63.58 m^3 (400 barrels) of CCTA that were prepared in line were used during the semi-industrial test time period, developed in this phase of the project (stability, combustion, fluid-dynamics, etc.).

Table 4. Average behavior operation variables

Summary	Average	Average	Total Average	EPA standard
Duty (percentage of total capacity)	65.00	60.00		
m^3/min*1000	2.00	1.93	1.96	
Furnace room temperature min (K)	1,330.00	1,411.00	1,584.00	
Temperature max (K)	1,668.00	1,683.00		
O% range	0.4 - 2.7	1.0 - 2.6	0.4 - 2.7	
O% average	1.70	1.70	1.70	
Vent temperature (K)	595.00	585.00	591.00	
R Qvat, vapor kg/Comb kg	78.40	79.60	78.80	
Atom. pressure Delta (kPa)	165.47	179.26	172.36	
Fuel Temperature	299.00	299.00	299.00	
Flame length (m)	1.22	1.22	1.22	
SO_2% (kg/m^3)	0.784	0.795	0.788	
Nox% (kg/m^3)	0.194	0.182	0.190	
CO% (kg/m^3)	0.115	0.96	0.108	
CO_2 (vol %)	14.90	14.70	14.80	
CO_2 (kg/MJoule)	85,580.00	86,010.00	86,010.00	
CO (kg/MJoule)	43.00	34.40	38.70	
NOx (kg/MJoule)	77.40	73.10	73.10	129.01
SO_2% (kg/MJoule)*	653.67	670.87	662.27	344.04
Part. material (kg/MJoule)**	976.21	1,079.42	1,010.61	43.00
Burner vapor pressure (kPa)	Average	496.42		
Burner comb. pressure (kPa)	Average	324.05		
Pump pressure (kPa)	Average	365.42		

* Gases without treatment
** Without electrostatic treatment, where 90% and 95% is eliminated and would meet the standard.

- Any liquid fuel burner could consume CCTA, provided an adequate nozzle is adapted.
- The "Peabody" nozzle was selected, with some modifications as for an efficient CCTA combustion. It could be observed that atomization with steam was more effective than with air.
- The CCTA complies with the Colombian Standard for sulfur content which has been limited to 1.7% in weight, the CCTA's content is 0.74% in weight.
- The SO_2 emissions, with no treatment to the fuel gases, are greater than those allowed by the EPA Standard which are limited to 344 kg/MJoules (0.8 lb/MMBTU) and those for the CCTA were 662.27 kg/MJoules (1.54 lb/MMBTU). These emissions could be significantly reduced with an emission control system.
- In the case of the Particulate Material the emission without any treatment is 1,011.61 kg/MJoule (2.35 lb/MMBTU) for the CCTA and the EPA Standard establishes a maximum of 43 kg/MJoule (0.1 lb/MMBTU). Electrostatic separators that show effi-

ciencies greater than 90% are commonly used in industry, reducing the particulate material emissions for the CCTA to values less than 86 kg/Mjoule (0.2 lb/MMBTU).

- As far as the emission of NO_x, the CCTA complies with the EPA standard which is 129.01 kg/MJoule (0.3 lb/MMBTU) and the average for the CCTA was 73 kg/Mjoule (0.3 lb/MMBTU).
- The NO_x and the SO_2 are less than those obtained for the fuel oil, Castilla crude and the Orimulsion.

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