

# THE SURFACE-ACTIVE BIO OIL SOLUTIONS IN SULFURED COPPER MINERAL BENEFIT

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**Abstract** - Surface-active bio-oil (SABO) solutions, prepared from vacuum pyrolysis bio-oil with a phenol-to-levoglucosan mass ratio of 4.8, was compared to pine-oil (PO) as foaming agent in the process of flotation of sulfured copper minerals. With the aid of  $2^3$  factorial designs, regression models were obtained for % Cu in flotation concentrate ( $L_{Cu}$ ) and % Cu recovery (R), as functions of foaming agent-to-Cu mineral, collector-to-Cu mineral mass ratio and liquid-to-solid ratio (v/w). Experimental designs composed of a  $2_{III}^{7-4}$  saturated design in its first half and a fold over  $2_{III}^{7-4}$  design in its second half allowed to study the influence of flotation conditions on  $L_{Cu}$  and R when SABO was the foaming agent. The factors selected were: particle size; pulp pH; flotation time; initial Cu content in the mineral (mineral type); liquid-to-solid ratio and finally SABO-to-mineral and collector-to-mineral mass ratio. Within the chosen experimental region only pulp pH affected significantly both responses. It is shown that high pulp pH, in the presence of minerals rich in Cu content leads to a significant increase in  $L_{Cu}$  and R. Although SABO to mineral mass ratio is high compared to PO, it is considered that an optimization study on pulp pH should reduce this difference making SABO an attractive alternative to PO and a way to widen the field of applications of pyrolysis products.

**Keywords:** Pyrolysis phenols; Bio oil.

## INTRODUCTION

The industrial biomass pyrolysis process has been applied since the beginning of the last century in order to obtain charcoal and chemicals. During the first half of twentieth century slow pyrolysis centered the main efforts of research and development studies, but short after this new pyrolysis processes became progressively better known (Beckman and Graham, 1994). Specially attractive appeared to be different process of fast pyrolysis (Diebold and Bridgwater, 1999) and vacuum slow pyrolysis (Roy et al., 1997; Boucher et al., 2000). The main objective of these new processes

is to obtain higher yields of a low degraded bio oil in order to use it as raw material for fuels (Radlein et al., 1996; Radlein, 1999; Shadix and Tenison, 1998), formaldehyde resins (Chum and Kreibich, 1993),  $NO_x$  and  $SO_x$  emission reduction (Zhou et al., 1997).

A low degraded bio-oil from vacuum slow pyrolysis of sugar cane bagasse has been used as a foaming agent to beneficiate sulfured Cu minerals (Brossard and Cortez, 1997). It is believed that there exists a relation between phenols and sugars contained in liquid products of sugar cane bagasse pyrolysis that plays an important role in the process of flotation of these minerals.

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It was observed that when used as a foaming agent, the pyrolysis fraction with highest phenol-to-levoglucosan mass ratio also has the great ability to raise  $L_{Cu}$  (Varela, 2002). Of the phenol constituents detected in pyrolysis liquids, p-cresol seemed to be the one that was primarily responsible for this behavior. These results obtained by us on a laboratory scale needed to be confirmed and compared to a commercial scaled up foaming agent. For this purpose it was conducted a bench scale study comprising the factors that could influence  $L_{Cu}$  and R in current industrial practice.

The factors taken into account were particle size, mineral pulp pH, collector-to-mineral mass ratio; flotation time, mineral type, foaming agent-to-mineral mass ratio, foaming agent age and liquid-to-solid ratio. This work is intended to contribute to the knowledge of possible applications of the pyrolysis process.

## MATERIAL AND METHODS

Experiments were conducted by means of a

discontinuous bench installation provided with a ball mill with a processing capacity of 0.8 kg of mineral pulp in 0.8 kg of water and a Denver flotation machine (2.5 L mineral pulp capacity). Sulfured copper mineral used in the bench tests was analyzed (see Table 1) with an atomic absorption spectroscopy AT I - UNICAM atomic absorption spectroscope.

### Flotation Reagents

Potassium amyl xanthate was used as collector and pH was regulated according to current industrial practice at Mina Grande El Cobre, with carbide ash, which is the solid residue of calcium carbide hydrolysis in acetylene gas production. The foaming agent was prepared from a bio-oil fraction, obtained from vacuum pyrolysis of air-dried bagasse (apparent density  $264 \text{ kgm}^{-3}$ ) at a speed rate of  $5.4 \text{ }^\circ\text{Cmin}^{-1}$  and 20 kPa at constant temperature ( $425 \text{ }^\circ\text{C}$ ) for 2 hours. The bio-oil fraction used had a phenol-to-levoglucosan mass ratio of 4.8 and the alkaline solution prepared from it, by mixing with 1 M NaOH, up to neutralization point had 25 % soluble solids.

**Table 1: Composition of copper mineral**

Component	Type of mineral		
	M-1	M-2	M-3
Ni	0.006	0.006	0.005
Co	0.002	0.004	0.003
Fe	9.2	10.26	8.56
Cu	2.19	2.23	1.15
Zn	0.012	0.014	0.007
Mn	0.141	0.137	0.084
Mg	1.0	1.02	0.06
Al	2.66	2.75	1.52
Ca	0.16	0.11	0.10
Cr	0.008	0.01	0.005
SiO <sub>2</sub>	0.07	0.095	0.039
SO <sub>4</sub> <sup>2-</sup>	9.56	11.97	7.02
S/BaSO <sub>4</sub>	3.19	7.32	4.01

## EXPERIMENTAL DESIGN

### SABO vs PO

(SABO) and PO as foaming agents for copper mineral flotation were compared by obtaining the

regression models  $L_{Cu}$  and for R under following experimental conditions:

- Foaming agent-to-mineral mass ratio;  $\text{gton}^{-1}$  (coded factor  $X_1$ )
- Collector-to-mineral mass ratio;  $\text{gton}^{-1}$  (coded factor:  $X_2$ )

- Liquid-to-solid ratio;
- $\text{mLg}^{-1}$  (coded factor:  $X_3$ ).

The regression models were obtained by processing experimental data from two  $2^3$  full factorial designs (Montgomery, 2001), one for each foaming agent. Higher (+1), and lower (-1) levels of these factors are shown in Table 2.

The following factors were kept constant:

- 55 % mineral pulp particles < 0.074 mm)
- pH = 10.6
- Copper mineral: M-3
- Flotation time: 8 minutes

Each  $2^3$  design had in addition four experiments at the center in order to determine  $S_{\text{Exp}}^2$ . The experimental matrix and responses appear in Table 3. Regression models for both foaming agents are shown in Table 4.

Determination of the influence of flotation conditions on  $L_{\text{Cu}}$  and R responses for SABO.

A convenient way to study the influence of several factors (in this case seven factors) on the response is by the fractional factorial experimental design (Barros Neto et al., 2001). In this case, the factors were  $X_{1f}$  = particle size,  $X_{2f}$  = pulp pH,  $X_{3f}$

collector-to-mineral mass ratio,  $X_{4f}$  = flotation time,  $X_{5f}$  = foaming agent-to-mineral mass ratio,  $X_{6f}$  = mineral type and  $X_{7f}$  = age of foaming agent.

The selected experimental design had sixteen runs and the first eight experiments were conducted according to a  $2_{\text{III}}^{7-4}$  saturated design with the following design conditions: (1)  $X_{4f} = X_{1f} X_{2f}$ , (2)  $X_{5f} = X_{1f} X_{3f}$ , (3)  $X_{6f} = X_{2f} X_{3f}$  and (4)  $X_{7f} = X_{1f} X_{2f} X_{3f}$  while the second half followed a fold over  $2_{\text{III}}^{7-4}$  saturated design with three of the former contrasts changed in sign, (5)  $X_{4f} = -X_{1f} X_{2f}$ , (6)  $X_{5f} = -X_{1f} X_{3f}$  and (7)  $X_{6f} = -X_{2f} X_{3f}$ . The fourth design condition was kept unchanged (4)  $X_{7f} = X_{1f} X_{2f} X_{3f}$ . Liquid-to-solid ratio was kept constant at 3.5 (v/w) taking into account the results obtained in the SABO versus PO comparison. This experimental arrangement allowed to obtain a Resolution IV fractional design in which non of the main effects are confounded with binary interactions effects and the higher order interactions are considered equal to zero (Montgomery, 2001). Factors, coded symbols and levels for the fractional designs are shown in Table 5.

**Table 2: Factors and levels for the two  $2^3$  full factorial designs for comparison of SABO and PO.**

		SABO		PO	
Factors	Coded	-1	1	-1	1
SABO to mineral mass ratio ( $\text{gton}^{-1}$ )	$X_1$	180	220	15	45
Collector-to-mineral mass ratio ( $\text{gton}^{-1}$ )	$X_2$	150	190	150	190
Liquid-to-solid Ratio ( $\text{mLg}^{-1}$ )	$X_3$	3.3	3.5	3.3	3.5

**Table 3: Experimental matrix and responses for the two  $2^3$  full factorial designs for comparison of SABO and PÓ.**

		Factors		SABO		PO	
Exp	$X_1$	$X_2$	$X_3$	$L_{\text{Cu}}$	R	$L_{\text{Cu}}$	R
1	-1	-1	-1	6.11	50.22	6.96	53.02
2	1	-1	-1	6.17	53.78	7.31	63.26
3	-1	1	-1	6.6	57.69	7.37	66.26
4	1	1	-1	7.15	61.39	7.52	71.10
5	-1	-1	1	6.24	55.08	7.17	59.80
6	1	-1	1	6.98	58.73	7.48	69.81
7	-1	1	1	7.19	61.68	7.57	72.72
8	1	1	1	7.59	63.39	7.78	79.50
9	0	0	0	6.68	57.35	7.26	62.71
10	0	0	0	6.75	56.72	7.37	66.25
11	0	0	0	6.57	55.65	7.43	67.19
12	0	0	0	6.66	58.02	7.30	63.99

**Table 4: -Regression models for  $L_{Cu}$  and R responses for SABO and PO in the  $2^3$  factorial designs.**

Foaming agent	Regression model	R-squared
SABO	(I) $L_{Cu} = 6.72 + 0.22X_1 + 0.38X_2 + 0.25X_3$	92.54%
PO	(II) $L_{Cu} = 7.38 + 0.13X_1 + 0.17X_2 + 0.11X_3$	91.90%
SABO	(III) $R = 57.48 + 1.58X_1 + 3.29X_2 + 1.98X_3$	94.50%
PO	(IV) $R = 66.30 + 3.98X_1 + 5.46X_2 + 3.52X_3$	93.41%

**Table 5: Factors, coded symbols and levels for the  $2_{III}^{7-4}$  design and the corresponding fold over  $2_{III}^{7-4}$  design.**

Factor	Symbol	Lower level (-1)	Higher level (+1)
Particle size (% Particles < 0.074 mm)	$X_{1f}$	40	60
Pulp pH	$X_{2f}$	9	12
Collector-to-mineral mass ratio ( $g\ ton^{-1}$ )	$X_{3f}$	130	230
Flotation time (min)	$X_{4f} = \pm X_{1f} X_{2f}$	8	16
Foaming agent-to-mineral mass ratio ( $g\ ton^{-1}$ )	$X_{5f} = \pm X_{1f} X_{3f}$	150	250
Type of mineral	$X_{6f} = \pm X_{2f} X_{3f}$	M1	M2
*Age of foaming agent	$X_{7f} = \pm X_{1f} X_{2f} X_{3f}$	E-1	E-2

\*E-1 Recently prepared SABO  
E-2 One-year-old SABO

## RESULTS AND DISCUSSION

As shown in Table 1, the composition of the three types of copper minerals used in this study is very similar for most of the constituents except for a rather low % Cu in mineral M-3. Planning and statistical data used for the comparison between SABO and (PO), appear in Tables 2 to 4. It is shown that all three factors taken into account ( $X_1$  = SABO-to-mineral mass ratio,  $X_2$  = collector-to-mineral mass ratio and  $X_3$  = liquid-to-solid ratio) are highly significant in relation to the studied responses for both foaming agents. On the other hand, Table 4 shows regression models as a function of the three significant factors for  $L_{Cu}$  and R when SABO (models I and III) or PO (models II and IV) is used as foaming agent in Cu flotation.

These models show a better performance for PO relative to R (model IV versus model III) and practically the same for  $L_{Cu}$ . (model I versus model II) Attention was turned now to the determination of the influence of flotation conditions on the performance of SABO. Results from this study are shown in Tables 5 to 8. As the number of factors to consider was high, it was used the fractional design approach, which consisted in running a

$2_{III}^{7-3}$  saturated factorial design combined with a fold over  $2_{III}^{7-3}$  design that had some of the contrasts changed in sign in order to obtain estimates of the main effects free of associations with binary interactions. This procedure was supported by the fact that at the defined experimental region, there was a linear relation between the factors and the studied responses. Due to this experimental arrangement the binary effects were annulated by the combinations of the design conditions (1) and (5), (2) and (6) and finally (3) and (7). In this way the precision of the response was increased (Resolution IV), allowing reliable results to be obtained. Factors coded symbols and levels are shown in Table 5. The experimental designs as well as the responses are shown in Table 6. The analysis of variance (Table 7 for  $L_{Cu}$  and Table 8 for R) conducted for the obtained results, show that the only significant factor was pulp pH ( $X_{2f}$ ) for both responses.

As the main components of SABO are water-soluble alkaline phenol salts, pulp pH regulation should be the most important factor regarding its foaming behavior. A regression analysis applied to these results, excluding non significant factors, show that for both responses the best results are obtained

when pulp pH operates at the higher level.

$$(V) L_{Cu} = 22.02 + 2.57 X_{2f}$$

$$(VI) R = 82.47 + 2.26 X_{2f}$$

Compared to the study between SABO and PO conducted at a fixed pulp pH of 10.26 and mineral

with low Cu content, when pH is raised to the higher level (pH equal to 12) and richer Cu minerals are used, both  $L_{Cu}$  and R are greatly improved as it can be seen by substituting the coded symbol  $X_{2f}$  by + 1. According to model (V)  $L_{Cu}$  would reach 24.59 % and model (VI) predicts a value of R of 84.73%. Both values are quite better than those obtained for SABO or even for PO in the comparative study.

**Table 6: Influence of flotation conditions on SABO behavior. Experimental matrix and responses for  $2_{III}^{7-4}$  design \* (experiments 1 to 8) and fold over  $2_{III}^{7-4}$  design\*\* (experiments 9 to 16).**

Exp N°	$X_{1f}$	$X_{2f}$	$X_{3f}$	$X_{4f}$	$X_{5f}$	$X_{6f}$	$X_{7f}$	$L_{Cu}$	R
1	-1	-1	-1	1	1	1	-1	18.49	78.14
2	1	-1	-1	-1	-1	1	1	21.25	81.28
3	-1	1	-1	-1	1	-1	1	22.31	82.73
4	1	1	-1	1	-1	-1	-1	22.78	83.59
5	-1	-1	1	1	-1	-1	1	19.72	79.12
6	1	-1	1	-1	1	-1	-1	21.02	80.59
7	-1	1	1	-1	-1	1	-1	24.69	85.45
8	1	1	1	1	1	1	1	24.39	84.45
9	-1	-1	-1	-1	-1	-1	-1	17.82	79.23
10	1	-1	-1	1	1	-1	1	18.04	80.15
11	-1	1	-1	1	-1	1	1	25.45	84.97
12	1	1	-1	-1	1	1	-1	26.9	85.78
13	-1	-1	1	-1	1	1	1	19.05	80.87
14	1	-1	1	1	-1	1	-1	20.23	82.33
15	-1	1	1	1	1	-1	-1	26.02	86.00
16	1	1	1	-1	-1	-1	1	24.22	84.91

$$* X_{4f} = X_{1f}X_{2f}; \quad X_{5f} = X_{1f}X_{3f}; \quad X_{6f} = X_{2f}X_{3f}; \quad X_{7f} = X_{1f}X_{2f}X_{3f}.$$

$$** X_{4f} = -X_{1f}X_{2f}; \quad X_{5f} = -X_{1f}X_{3f}; \quad X_{6f} = -X_{2f}X_{3f}; \quad X_{7f} = X_{1f}X_{2f}X_{3f}.$$

**Table 7: Analysis of variance for  $L_{Cu}$  from composed  $2_{III}^{7-4}$  fractional factorial design for SABO flotation conditions**

Source of variation	Sum of Squares	Df	Mean Square	F-ratio	p-value
$X_{1f}$	1.7424	1	1.7424	0.73	0.4175
$X_{2f}$	105.7810	1	105.7810	44.37	0.0002
$X_{3f}$	2.4806	1	2.4806	1.04	0.3376
$X_{4f}$	0.2862	1	0.2862	0.12	0.7379
$X_{5f}$	0.0002	1	0.0002	0.00	0.9925
$X_{6f}$	4.5369	1	4.5369	1.90	0.2051
$X_{7f}$	0.7744	1	0.7744	0.32	0.5844
Total error	19.0738	8	2.3842	-	-
-	134.6760	15	-	-	-

**Table 8: Analysis of variance for R from composed  $2_{III}^{7-4}$  fractional factorial design for SABO flotation conditions.**

Source of variation	Sum of Squares	Df	Mean Square	F-ratio	p-value
X <sub>1f</sub>	2.6978	1	2.6978	2.00	0.1950
X <sub>2f</sub>	81.7668	1	81.7668	60.62	0.0001
X <sub>3f</sub>	3.8514	1	3.8514	2.86	0.1295
X <sub>4f</sub>	0.2730	1	0.2730	0.20	0.6647
X <sub>5f</sub>	0.2943	1	0.2943	0.22	0.6529
X <sub>6f</sub>	3.0189	1	3.0189	2.24	0.1730
X <sub>7f</sub>	0.4323	1	0.4323	0.32	0.5868
Total error	10.7900	8	1.3488	-	-
Total (corr.)	103.125	15	-	-	-

## CONCLUSIONS

SABO prepared from a vacuum pyrolysis bio-oil fraction with a high phenol-to-levoglucosan mass ratio i.e. 4.8 constitutes an alternative of effective foaming agent for the benefit of sulfured copper minerals. This product works well at high pulp pH level and requires approximately the same flotation conditions as PO. Although it must be added with a higher foaming agent-to-mineral mass ratio than PO, an optimization study on pulp pH levels should reduce this difference making SABO an attractive alternative to PO.

These results could help to widen the field of applications of pyrolysis products.

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## NOMENCLATURE

Corr	Corrected sum of squares
Df	Degrees of freedom
F-test	F statistic
L <sub>Cu</sub>	% Cu in flotation concentrate
p value	Real significance level
PO	Pine oil
R	% Cu recovery from original mineral
R squared	Coefficient of determination
SABO	Surface active bio oil
X <sub>1</sub> , X <sub>2</sub> and X <sub>3</sub>	Coded factors for SABO vs. PO

comparison with a  $2^3$  full factorial design.

X<sub>1f</sub>, X<sub>2f</sub>, ...X<sub>7f</sub> Coded factors for fractional experimental design

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