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Dissolved air flotation: A novel approach to recovery of organosolv lignin

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ABSTRACT

A novel method of organosolv lignin recovery, consisting of simultaneous precipitation and dissolved air flotation (DAF), is proposed. DAF offers a low energy, low maintenance alternative to centrifugation and filtration. DAF of organosolv lignin is studied in order to determine the parameters resulting in the fastest settling and most complete precipitation. Temperature, mixing regime and air saturation pressure were found to be important parameters. Higher temperature resulted in faster settling, but lower final lignin yields at temperatures above 30 °C. At 40 °C lignin formed a fine precipitate that did not clarify. Rapid addition of black liquor to water resulted in faster clarification. This is due to a redistribution of micro-bubbles in the dilution water immediately prior to formation of precipitate. Higher air saturation resulted in faster clarification. The difference was more pronounced if black liquor addition rate was slow.

1. Introduction

Conversion of lignocellulosics into fuel ethanol has recently received international attention. The process is reliant on the conversion of cellulose into sugars using cellulase enzymes. Lignin, contributing 15–25% of hardwood dry mass, inhibits the action of cellulase in several ways. Lignin competitively absorbs cellulase enzymes and, along with hemicellulose, forms a complex acting as a physical barrier between cellulose and cellulase enzymes [1,2].

Lignin is also reported to be a potential raw material for the production of plastics, adhesives and resin additives [3]. The forest refinery concept, also referred to as biorefining, has been described as the separation and recovery of cellulose, hemicellulose and lignin as cleanly as possible [4]. Conventional pulp and paper mills simply burn the lignin for its heat value. The value of lignin when used as a boiler fuel is estimated at 18 c/kg compared to a conservative estimate of 108 c/kg if lignin is used for other products [5]. As a replacement for phenol in resin it has a potential value of 151 c/kg [6] (all figures adjusted for inflation). It is therefore important to the economics of bioethanol production to produce a high quality lignin product. Organosolv delignification is one such source of high quality, unmodified lignin containing many reactive side chains for further chemical modification [3,7].

Organosolv pulping uses an organic solvent, commonly ethanol solutions of 30–70% (v/v), at temperatures of 150–190 °C to dissolve lignin and hemicelluloses sugars from wood leaving cellulose relatively unchanged. The lignin macromolecule is depolymerised at temperatures above 140 °C and is soluble in the organic solvent. The rate of delignification can be increased by increasing temperature or lowering the pH of the liquor [8,9]. Small amounts (~0.1%, w/w) of sulphuric acid are often used to lower the pH. However, altering the conditions of organosolv pulping also alters the chemical composition of the lignin recovered [10]. The solution (black liquor) containing lignin and hemicelluloses sugars can be concentrated slightly by flashing to atmospheric pressure. Diluting black liquor with acidified water precipitates the lignin, which can then be centrifuged and recovered. Botello et al. [11] determined that the greatest dilution and lowest pH resulted in the best lignin recovery yields although pH has a minimal effect.

Filterability of precipitated ethylene glycol lignin was considered a problem due to the high viscosity of the solvent. Dilution, acid concentration and filtering temperature were studied. Liquor to acidified water ratio of 1:3 and filtering temperature of 50–60 °C were the optimum conditions for high yield of lignin while maintaining adequate lignin properties [12].

Centrifugation of precipitated lignin, as described in patents by Diebold et al. [13] and Lora et al. [14], has been met with aversion, perhaps due to high maintenance costs. Centrifugation of precipitated lignin is performed only after a slow preliminary settling step.

Foam fractionation of Kraft lignin is reported to be ineffective [15,16]. However, foam flotation of Kraft lignin precipitated with aluminium salts can be effected with careful control of the pH [16]. Wang et al. [15] reports that foam fractionation of Kraft lignin without a precipitating agent or a collector results in only 27% lignin removal at the optimal superficial gas velocity. The

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addition of an alum precipitator ($Al_2(SO_4)_3$) prior to foam flotation gave only 12% lignin recovery. A collector was necessary to endow lignin–alum flocs with hydrophobic surfaces, allowing bubble adherence.

The hydrophobic nature of organosolv lignin makes flotation an ideal method of separation. This paper identifies dissolved air flotation (DAF) as the most appropriate technique in order to eliminate floc destabilisation caused by turbulence. Micro-bubbles are formed in DAF by the reduction in pressure of water pre-saturated with air. When the air saturated water is forced through an orifice or needle valve, a cloud of bubbles in the size range 30–100 μm are formed. These bubbles attach to flocs of particles in solution and the bubble and attached solids rise due to buoyancy. DAF is used extensively in minerals and wastewater processing [17,18].

The use of dissolved air flotation for the separation of ethanol pulping lignin from diluted black liquor is a novel approach to lignin recovery. In this paper, the effects of mixing regime, dilution ratio, solution temperatures, HCl concentration, saturation pressure and final ethanol concentration are examined using fractional factorial design.

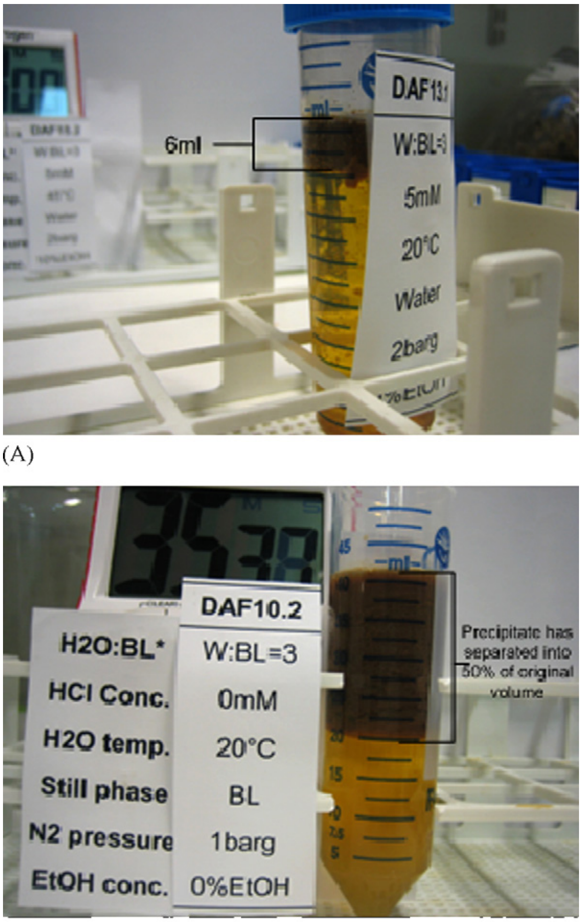
2. Methods

2.1. Procedure

In each experiment, black liquor was diluted in a falcon flask by 2, 3 or 7 times. The black liquor was produced by autocatalysed organosolv pulping of chipped *Salix schwerinii* at 185 °C for 3 h at a solid:liquid ratio of 11 as previously described [19]. The volume of black liquor diluted was 5, 10 or 13.3 ml when using a water to black liquor ratio of 7, 3 or 2 respectively. This resulted in a final volume of 40 ml for each experiment. Solutions were prepared from deionised water containing each of the four combinations of 0 or 5 mM of HCl and 0 or 10% ethanol. These solutions, intended to dilute the black liquor, were heated to the appropriate temperature using a water bath and saturated with gas by shaking in a sealed falcon tube, pressurised from a nitrogen cylinder to the desired pressure. On starting an experiment, the appropriate solution was removed from pressure, mixed with black liquor under one of two mixing regimes and placed upright while a stop clock was simultaneously started. A photo record of the flotation process was made by taking frequent photos using a digital camera at a defined orientation to the falcon tube.

2.2. Experimental design

The first set of experiments was designed as a 2^{6-2} fractional factorial design to determine the effect of six parameters on both final flotation volume of lignin and 50% clarification time. Final flotation volume was defined as the volume that was occupied by the floating precipitate after at least 24 h as shown in Fig. 1A. It was assumed that the equilibrium volume of lignin was proportional to its mass and therefore a measure of final yield. This method is not precise and is therefore only used in the first block of experiments as a screening test for yield. Further yield measurements were conducted using filtered weight of precipitate. 50% clarification time was defined as the time elapsed between diluting the black liquor and 50% of the volume of the diluted liquor becoming clear as shown in Fig. 1B.



(A)

(B)

Fig. 1. (A) Final flotation volume of 6 ml and (B) 50% clarification time of 35 min 37 s.

Parameters and their value at each level are shown in Table 1. Table 2 shows the level of each parameter for the 16 experiments, which were carried out in duplicate. One of two mixing regimes is indicated by the “still phase”. If the still phase is water, the water is added to the falcon tube and then the black liquor is delivered into it using a syringe. If the stationary phase is labelled BL, the black liquor is first added to the falcon tube and the water is decanted into the black liquor.

Following the first set of experiments, it became apparent that temperature has a significant effect on both yield and clarification time. Samples at 45 °C water temperature resulted in a very fine precipitate, which settled very slowly if at all. Accurate determination of 50% clarification time was not possible. The effect of the temperature increase on final floated volume was a decrease from 4.9 to 1.7 ml. The strong effect of temperature masked the effect of other parameters. However, other observations from this block of experiments were as follows; high ethanol concentration and low water to black liquor ratio resulted in incomplete precipitation. The

Table 1
Low and high level values of parameters in the first set of fractional factorial designed experiments

	H_2O:BL[a]	HCl concentration (mM)	H_2O temperature (°C)	Still phase	N_2 pressure (psig)	EtOH concentration
Low level	2	0	20	Water	14	0
High level	3	5	45	BL[a]	28	10

[a] Black liquor.

Table 2
Parameter levels of each run in the first set of fractional factorial designed experiments

Run #	H_2O:BL[a]	HCl concentration	H_2O temperature	Still phase	N_2 pressure	EtOH concentration
1	−1	−1	−1	−1	+1	+1
2	−1	−1	−1	+1	+1	+1
3	−1	−1	+1	−1	+1	−1
4	−1	−1	+1	+1	+1	−1
5	−1	+1	−1	−1	−1	+1
6	−1	+1	−1	+1	−1	+1
7	−1	+1	+1	−1	−1	−1
8	−1	+1	+1	+1	−1	−1
9	+1	−1	−1	−1	−1	−1
10	+1	−1	−1	+1	−1	−1
11	+1	−1	+1	−1	−1	+1
12	+1	−1	+1	+1	−1	+1
13	+1	+1	−1	−1	+1	−1
14	+1	+1	−1	+1	+1	−1
15	+1	+1	+1	−1	+1	+1
16	+1	+1	+1	+1	+1	+1

[a] Black liquor.

Table 3
Low and high level values of parameters in the second set of fractional factorial designed experiments

	H_2O:BL	Time to addition (s)	N_2 pressure (psig)	BL temperature (°C)	HCl concentration (mM)
Low level	3	4	5	20	1
High level	7	8	15	25	5

use of HCl increased final flotation volume slightly. Using water as stationary phase resulted in a clarification time 8.5 min faster than a black liquor stationary phase if all high temperature experiments were given the same arbitrarily large settling time (denoting that these samples did not settle after 24 h). Increasing nitrogen pressure had no significant effect on either output variable.

In light of these observations, 3 further sets of experiments were performed as outlined below. The temperature and addition speed were examined to illustrate the variables affecting clarification rate. Finally, a second factorial block was designed to examine variables that may be affecting final yield.

(1) The temperature was studied in isolation using a water to black liquor ratio of 3, HCl concentration of 0 mM, water as the still phase, a nitrogen pressure of 14 psig and no ethanol in the water solution. Temperatures studied were 0, 5, 10, 15, 20, 25, 30, 35 and 40 °C.

(2) The first block of experiments showed that a water stationary phase resulted in faster clarification. It was also apparent that the rate of addition of black liquor to water was a significant noise variable. For this reason, it was decided to examine the effect of addition rate and nitrogen pressure on settling time in order to show the effect of a fine dispersion of micro-bubbles during precipitation. A temperature of 20 °C was used for all addition rate experiments. The levels of addition rate were 5 and 10 ml/s. The pressure levels were 15 and 30 psig.

(3) A second set of factorial designed experiments was then undertaken at constant water temperature to study effects of HCl concentration, water to liquor ratio, nitrogen pressures, black liquor temperature and time to addition. Time to addition is defined as the time elapsed between removing the water from the nitrogen pressure and delivering the black liquor. In this set of experiments, the rate of addition was 10 ml/s and the temperature was 20 °C. Table 3 shows the value of high and low levels of each parameter. Table 4 shows the level of each parameter in each of 8 experiments, which were carried out in duplicate.

In all experiments following the first set of factorial experiments, 50% clarification times and lignin yields by mass of filtered precipitate were measured. All experiments were performed in duplicates.

3. Results and discussion

(1) Temperature had a minor affect on yield up to a temperature of 20 °C. From 20 °C onwards, filtered yield declined as temperature increased. At 20 °C, the settling time is short and the reduction in yield is only 3.5% of the maximum. Further experiments are therefore performed at 20 °C. Temperature has a significant effect on settling time as shown in Fig. 2. Settling time decreased with increasing temperature up until 35 °C, after which it was impossible to discern a precipitate interface because most of the lignin formed a very fine precipitate that

Table 4
Parameter levels of each run in the second set of fractional factorial designed experiments

Run #	H_2O:BL	Time to addition	N_2 pressure	BL temperature	HCl concentration
1	−1	−1	−1	+1	+1
2	−1	−1	+1	+1	−1
3	−1	+1	−1	−1	+1
4	−1	+1	+1	−1	−1
5	+1	−1	−1	−1	−1
6	+1	−1	+1	−1	+1
7	+1	+1	−1	+1	−1
8	+1	+1	+1	+1	+1

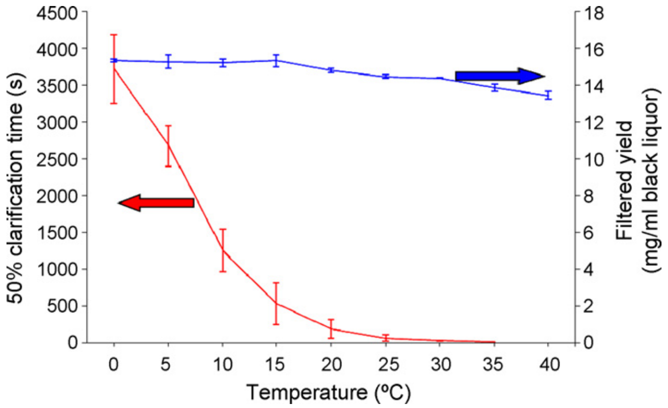


Fig. 2. Effect of temperature on clarification time and final filtered yield during dissolved air flotation of organosolv lignin.

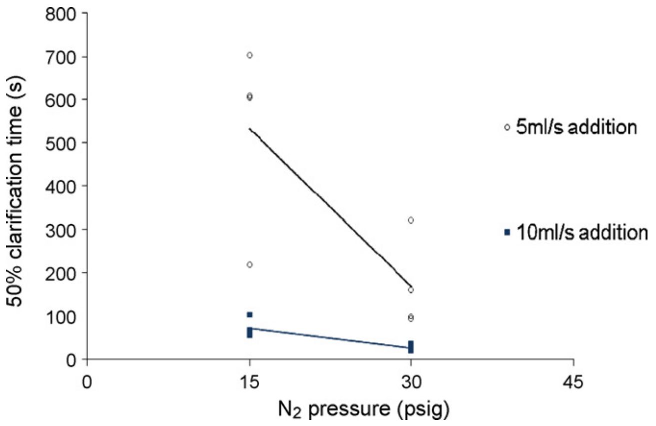


Fig. 4. Faster black liquor addition results in faster clarification. Higher pressure causes faster clarification and is more pronounced at a lower addition rate.

remained in suspension. This is illustrated in Fig. 3. As temperature increased, the colour of the supernatant after 24 h darkened.

Flotation efficiency relies on the collision efficiency between particles and bubbles. Collision efficiency has been shown to increase with increasing floc size, assuming consistent electric chemical properties of the bubble and the particle [20]. According to the trajectory model of Han [21], collision efficiency increases as floc size approaches the mean bubble size. Collision efficiency is low when particle size is much smaller than bubble size. This is partly due to a reduction in mass of the particles thereby reducing inertial impaction. At temperatures above 35 °C, the precipitate formed is extremely fine and does not flocculate. The formation of this fine precipitate may be due to homogeneous nucleation. Temperature and pressure also affect bubble size. Bubble growth is faster at higher temperatures resulting in larger bubbles with greater volume to projected area ratio and therefore faster rising due to buoyancy. This would account for the increased speed with increased temperature up until the point at which the lignin flocs are too small to attach to a bubble.

(2) The effect of addition rate and nitrogen pressure is evident from Fig. 4.

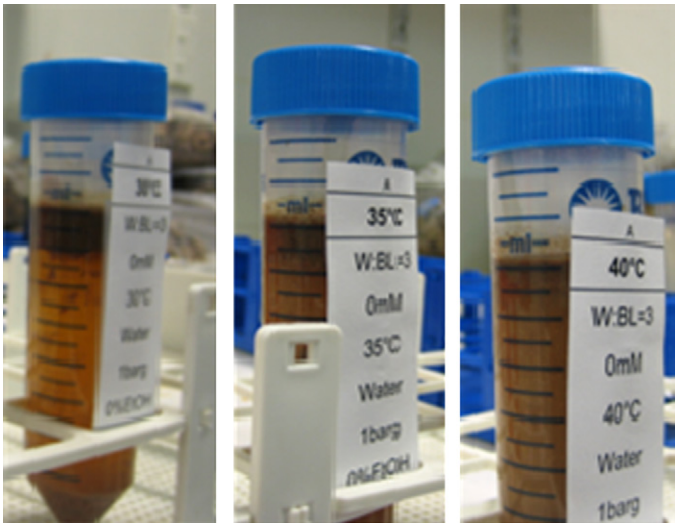


Fig. 3. Precipitates 24 h after dilution. At 30 °C (far left), an interface is visible. At 40 °C (far right), no floated precipitate can be distinguished from the continuous phase.

The rising velocity depends on the presence of buoyant micro-bubbles attached to the precipitate. Black liquor addition rate and pressure are variables that determine the dispersion of micro-bubbles during precipitation of black liquor. At the high addition rate of 10 ml/s, the micro-bubbles that have formed when pressure is quickly reduced and floated to the top of the water are redistributed by aggressive mixing caused by squirting the black liquor into the water. The 5 ml/s addition rate does not cause enough mixing to redistribute the micro-bubbles formed. Also, lignin may agglomerate more due to the turbulent energy applied during fast mixing, increasing floc size and improving collision efficiency. At the 15 psig pressure level, fewer micro-bubbles are nucleated to attach to precipitated lignin as it forms. At low addition rate and high pressure, the settling velocity is still fast because more micro-bubbles nucleate due to the higher gas saturation at 30 psig compared to 15 psig. Increased pressure results in a greater number of bubbles and smaller average bubble diameter. Image analysis has shown that average bubble size is 71 μm using saturation pressure of 29 psi and 32.4 μm using a saturation pressure of 73 psi [22]. Thus, higher pressure results in greater frequency of attachment and greater buoyancy.

The ideal conditions for rapid separation of precipitated lignin are high temperature, high water saturation pressure and fast addition of black liquor in order to redistribute micro-bubbles during precipitation. It should be noted that precipitation followed by pressurisation to 30 psig, thorough mixing and pressure relief resulted in incomplete flotation and times similar to that of 5 ml/s addition at 30 psig. This suggests that faster clarification is achieved when micro-bubbles attach to the precipitate during precipitate nucleation.

(3) Increasing the pressure from 5 to 15 psig reduced the 50% clarification time by 22 s. A higher water to black liquor ratio resulted in faster clarification due to less precipitate being present resulting in lower steric hindrance during settling. HCl concentration may result in a small reduction in clarification time. None of the variables examined had an effect on the filtered yield of lignin.

To apply dissolved air flotation of organosolv lignin in an industrial process, the addition of black liquor to nitrogen saturated water should be performed with turbulent addition of the black liquor into room temperature water with sufficient nitrogen saturation. It is critical that the final temperature of the diluted black liquor is below 35 °C to avoid the fine precipitate formation described. Black liquor from the organosolv process is typically at a temperature of 80–100 °C after flashing at atmospheric pressure. The final temperature after dilution can be reduced in several ways:

(1) Cooling of the black liquor either by heat exchanger or vacuum flashing prior to dilution.
(2) Sub-cooling of the diluting water prior to dilution.
(3) Increasing the water to black liquor ratio.

The third option is the most elegant and economical of these. However, the subsequent recovery of ethanol will be more energy intensive. This can be somewhat alleviated by distillation of the black liquor to the maximum lignin concentration before dilution.

4. Conclusions

Dissolved air flotation is an effective method of recovering organosolv lignin precipitate without the need for precipitating or collecting agents. Efficient flotation and good clarification of organosolv lignin occurs at temperatures below 35 °C. Above 35 °C, the precipitate formed does not flocculate and is too small to attach to micro-bubbles. Fastest flotation occurs when saturation pressure is high and black liquor–water mixing is rapid resulting in the redistribution of micro-bubbles during floc formation. Higher saturation pressure can reduce the effect of slow addition rate due to the formation of more bubbles of smaller size.

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References

[1] N. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapple, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, Bioresource Technology 96 (2005) 673–686.
[2] R. Sutcliffe, J.N. Saddler, Role of lignin in the adsorption on cellulases during enzymatic treatment of lignocellulosic material, in: Biotechnology and Bioengineering Symposium, John Wiley & Sons, 1986.
[3] J.H. Lora, W.G. Glasser, Recent industrial applications of lignin: a sustainable alternative to non-renewable materials, Journal of Polymers and the Environment 10 (2002) 39–47.
[4] R.C. Myerly, M.D. Nicholson, R. Katzen, J.M. Taylor, The Forest Refinery, ChemTech 11 (1981) 186–192.
[5] R. Aravamuthan, W.Y. Chen, K. Zargarian, G. April, Ethanol from southern hardwoods: the role of presulphonation in the acid hydrolysis process, in: Biotechnology and Bioengineering Symposium, John Wiley & Sons, 1986.
[6] J.D. Wright, A.J. Power, Concentrated halogen acid hydrolysis processes for alcohol fuel production, in: Biotechnology and Bioengineering Symposium, John Wiley & Sons, 1986.
[7] J.J. Meister, Modification of lignin, Journal of Macromolecular Science-Polymer Reviews C42 (2002) 235–289.
[8] T.N. Kleinert, Ethanol–water delignification of wood-rate constants and activation-energy, Tappi Journal 58 (1975) 170–171.
[9] K.V. Sarkanen, Acid-catalysed delignification of lignocellulosics in organic solvents, in: K.V. Sarkanen, D.A. Tillman (Eds.), Progress in Biomass Conversion, Academic Press, 1980, pp. 127–144.
[10] M. Oliet, F. Rodriguez, J. Garcia, M.A. Gilarranz, The effect of autocatalyzed ethanol pulping on lignin characteristics, Journal of Wood Chemistry and Technology 21 (2001) 81–95.
[11] J.I. Botello, M.A. Gilarranz, F. Rodriguez, M. Oliet, Recovery of solvent and by-products from organosolv black liquor, Separation Science and Technology 34 (1999) 2431–2445.
[12] R.W. Thring, E. Chornet, R.P. Overend, Recovery of a solvolytic lignin—effects of spent liquor acid volume ratio, acid concentration and temperature, Biomass 23 (1990) 289–305.
[13] V.B. Diebold, W.F. Cowan, J.K. Walsh, Solvent pulping process, 1978, CP Associates Ltd., US Patent 4,100,016.
[14] J.H. Lora, R. Katzen, M. Cronlund, C.F. Wu, Recovery of lignin, 1988, Repap Technologies Inc., US Patent 4,764,596.
[15] M.H. Wang, Granstro, T.E. Ml, L.K. Wilson, Wang, Removal of lignin from water by precipitate flotation, Journal of the Environmental Engineering Division-ASCE 100 (1974) 629–640.
[16] H. Nakayama, E. Matijevic, K. Shinoda, Precipitation and micro-flotation of Kraft lignin and hemoglobin, Journal of Colloid and Interface Science 61 (1977) 590–599.
[17] J. Rubio, M.L. Souza, R.W. Smith, Overview of flotation as a wastewater treatment technique, Minerals Engineering 15 (2002) 139–155.
[18] R.T. Rodrigues, J. Rubio, DAF-dissolved air flotation: potential applications in the mining and mineral processing industry, International Journal of Mineral Processing 82 (2007) 1–13.
[19] H. Belanger, R.L. Prestidge, T.J. Lough, J.D. Watson, J.-L. Yao, Process for the production of biofuel from plant materials, in: USPTO, BioJoule Ltd., 2007.
[20] J.K. Edzwald, Principles and applications of dissolved air flotation, Water Science and Technology 31 (1995) 1–23.
[21] M.Y. Han, Modeling of DAF: the effect of particle and bubble characteristics, Journal of Water Supply Research and Technology-AQUA 51 (2002) 27–34.
[22] M. Han, T.I. Kim, J. Kim, Effects of floc and bubble size on the efficiency of the dissolved air flotation (DAF) process, Water Science and Technology 56 (2007) 109–115.