© Triveni Enterprises
Vikas Nagar, Lucknow, INDIA
editor@jeb.co.in
Full paper available on: www.jeb.co.in

J. Environ. Biol.
33, 941-944 (2012)
ISSN: 0254 - 8704
CODEN: JEBIDP

Environmental friendly alkaline sulfite anthra quinone-methonal (ASAM) pulping with *Rumex crispus* plant extract of woody materials

Author Details

Gulnur Mertoglu- Elmas *(Corresponding author)*	Istanbul University, Faculty of Forestry, Bahcekoy-34473, Istanbul, Turkey e-mail : mertoglug@istanbul.edu.tr
Keriman Gunaydin	Istanbul University, Faculty of Sciences, Molecular Biology and Genetic, Beyazit-34473, Istanbul, Turkey
Oznur Ozden	Istanbul University, Faculty of Forestry, Bahcekoy-34473, Istanbul, Turkey

Publication Data

Paper received:
25 March 2011

Revised received:
20 August 2011

Accepted:
16 October 2011

Abstract

ASAM with *Rumex crispus* extract organosolv pulping was developed by using 1,5-dihydroxy-3-methoxy-7-methyl-anthraquinone from *Rumex crispus* root, instead of anthraquinone. ASAM was also produced as a control pulping. Both pulps were made by handsheets from fast growing *P.deltoides* clone (*Samsun p.clone*), *Robinia pseudoacacia* L. and *Pinus pinaster* grown in Turkey for wood fibrous raw materials. The mechanical consisting tensile, bursting and tear values and optical values of ASAM handsheets yellowness, brightness and whiteness were compared to ASAM with *Rumex crispus* L. extracted. It is concluded that ASAM with *Rumex crispus* extract pulping suits well in the manufacturing of special papers.

Key words

Rumex crispus extract, 1,5-dihydroxy-3-methoxy-7- methylanthraquinone, *Populus deltoides* (Samsun p.clone), *Robinia pseudoacacia* L., *Pinus pinaster,* Organosolv pulp.

Introduction

Chemical pulping used in the pulp and paper industry is varied from strongly alkaline (kraft) to acidic (Gullichsen, 2000). Sulfite and Kraft cooking methods including alkaline and acidic components sulfurous components, contained especially, inside free hazardous emissions cause serious environmental pollution (Stockburger, 1993; Shatalov and Pereira, 2001). That's why pulp and paper industry is considered as one of the worst environmental pollutants. Expensive investments and an ever increasing work force are somewhat needed in order to decrease the environmental pollution to reasonable levels and to control the sustainability (Black, 1991; Patt *et al*., 1998).

In recent years, researchers have begun studying the solvent based, environmentally friendly chemical pulping methods, which are likely to replace the currently known conventional pulping processes, which are considered as less harmful to environment. At the same time, it is also expected to become applicable compared to kraft pulping in rather smaller scales. Another purpose, on the other hand, is to benefit the maximum gain from the woody biomass (Patt *et al*., 1998).

In pulp and paper industry, ASAM cooking method containing the alkaline sulfite- anthraquinone-methanol cooking solution is widely used as an alternative method methanol, as well as chemical gain from ASAM pulping solution, decreases the unit expenses in paper production (Patt *et al.*,1994; Zimmermann *et al.*,1991; Patt *et al.*, 1998).

The foremost benefits of ASAM pulping can be listed as; not entirely depended upon one particular raw material (hardwood, softwood and non-wood materials are all equally usable), sustaining high productivity and causing rather less environmental pollution, that's why it is considered as environmentally friendly (Patt *et al.*,1994; Patt *et al.*, 1998).

Rumex crispus (Turkish named Labada) is a perennial plant growing to 150 cm at most. Its basal leaves are narrowly lanceolate to oblanceolate, also more than 3 times longer than the width and sharp (Davis, 1965-1985). The plants can be found in banks, marshes and waste places. Its flowering season starts from May to August and it can be found in the many provinces of Turkey (Davis, 1965-1985; Yaltirik and Efe, 1989).

A yellow colored pigment which is an anthraquinone derivative, 1.5-dihydroxy-3-methoxy-7-methyl-anthraquinone can be extracted from the lumped roots (Baskan *et al.*, 2007). The purpose of the study was to observe the effect of ASAM with *Rumex crispus* extract pulping process on the productivity, pulp and properties, and to compare with the control ASAM produced under the same conditions.

Materials and Methods

P. deltoides clone (5 year-old Samsun p. clone) from in the plantation area of the poplar and Fast Growing Forest Trees Research Institute of Izmit, Turkey, *Robinia pseudoacacia* L. and *Pinus pinaster* samples as a raw woody material were prepared in industrial chip size (1-2 cm length, 1.5-4 mm thickness, 1cm width).

Pulping rates : After the preparation stage, the chips were put into a 10 l rotating laboratory digester pretreated by steaming and then pulped. Cooking liquor's composition and pulping conditions of control ASAM and ASAM with *Rumex* extract are given in Tables 1 and 2. In addition to values of table according to the relationship between chips and white liquor, the required amount of water was added to maintain wood to liquid ratio at 1:6, AQ (anthraquinone) and *Rumex crispus* extract 0.1 %, methanol 10 % and the highest temperature was 170 °C as dependent parameters.

Testing of laboratory handsheets: ASAM with *Rumex crispus* pulp obtained from *P.deltoides* clone, *Robinia pseudoacacia* and *Pinus pinaster* woody samples to save energy and to decrease pulping time were pulped through refiner which had Sprout–Waldron type labor scale with one disc. Handsheets were obtained from unbleached pulps and according to the TAPPI and ISO test standard methods (Tappi test methods, 1992–1993), "Preparation of laboratory sheets for physical testing—Part 2: Rapid-Kothen method" (ISO 5269-2:2004). The strength properties were determined following standard methods: pulp- determination of drainability Schopper Riegler °SR (ISO 5267-1:1999), paper, board and pulps-standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples (ISO 187:1990), grammage (ISO 536:1995), moisture (ISO 287:2009), thickness and density (TAPPI T 411 om-89), tensile index (ISO 1924-2:1994), tearing resistance (ISO 1974:1990), bursting strength (ISO 2758:2001). Optical properties like opacity (ISO 2471:1998), ISO brightness (ISO 2470-2:2008), yellowness index (ASTM E-313) were also tested according to ISO standards with 3300 type Elrepho spectrophotometers.

Results and Discussion

During the process of ASAM pulpings, time taken was approximately 120-170 min. The correlation between temperature and pressure ASAM with *Rumex* extract pulping showed that with pressure increase the temperature didn't increase at first, but came up to 170 °C and kept on slightly increasing in the process of *Robinia pseudoacacia* sample ASAM with *Rumex* extract pulping were made in more than a 240 minute process. ASAM with *Rumex* extract pulping of samples coming up to a maximum temperature were spent more process than those of ASAM pulping. It was concluded that *Rumex* extract caused this situation.

The total yield for ASAM unbleached pulp was highest (58 %) in the *P.deltoides* clone wood and lowest (48 %) in *Pinus pinaster* wood. ASAM with *Rumex crispus* extract pulp was also found highest (51 %) in *P.deltoides* clone and least (48 %) in *Pinus pinaster*. The total yield for ASAM pulps were higher than those of ASAM with *Rumex* extract pulps.

The strength and optical properties of the ASAM with *Rumex* extract and the control ASAM pulps obtained from *P.deltoides* clone, *Robinia pseudoacacia* and *Pinus pinaster* woody materials are shown in Table 2 and 3.

Tensile strength is a basic measure showing the applicability of handsheets in paper industry. Tensile index of ASAM handsheets was found highest (67.7N.m g^{-1}) in *Pinus pinaster* and least (43.4 N.m g^{-1}) in *Robinia pseudoacacia.* ASAM with *Rumex* extract handsheets was also determined highest (53 N.m g^{-1}) in *Pinus pinaster* and least (32 N.m g^{-1}) in *Robinia pseudoacacia* (Table 2). When ASAM with *Rumex* extract handsheets compared to the ASAM ones, *Pinus pinaster* ASAM handsheets had been highest and

Table- 1: Conditions of ASAM with *Rumex* extract pulping for some wood samples

Raw material	Na_2SO_3 / NaOH (%)	Time (min)	Max T (°C)	Max P. (bar)	Pulp Y %	White L. pH	Black L.pH	°SR
P. deltoids clone	3.63	120	170	12.5	51	12	8.12	23
Robinia pseudoacacia .	3.63	240	165	13.5	48	12	9.3	24
Pinus pinea	5.39	75	165	13.5	49	12	8.9	15

Pulp Y : Pulp Yield ; Max T: maximum temperature; White L.pH: White Liquor pH ; Max P: maximum pressure ; Black L.pH: Black Liquor pH ; °SR **:** Schopper-Riegler number of pulp

Table- 2: The strength properties of the control and ASAM with *Rumex* extract pulps.

Raw material	Thickness (μm)	Grammage (g m^{-2})	Tensile index (N m g^{-1})	Tear index (mN m^2 g^{-1})	Bursting kPa m^2 g^{-1}
*ASAM *P.deltoides clone*	128.3	94.7	59.4	3.8	4.8
*ASAM *Robinia pseudoacacia*	160.2	96.4	43.4	2.8	2.5
*ASAM *Pinus pinaster*	132.5	92.5	67.7	6.7	6.8
**ASAM *P.deltoides clone*	173.0	98.4	42.0	3.1	2.3
**ASAM *Robinia pseudoacacia*	156.3	91.1	32.0	2.3	1.6
**ASAM *Pinus pinaster*	117.5	84.2	53.0	5.6	5.3

*Control ASAM; ** ASAM with Rumex extract

Table- 3: The optical properties of the control and ASAM with *Rumex* extract pulps (%).

Samples	Brightness	Opacity	Whiteness		Transparency	Yellowness
			W	T		
*ASAM *Pinus pinaster*	31.47[1]	93.46[1]	-61.0[1]	-20.20[1]	22.78	33.70[1]
*ASAM *P.deltoides clone*	45.89[1]	96.92[1]	-7.30[1]	-11.10[1]	14.41	21.30[1]
* ASAM *Robinia pseudoacacia L.*	34.66[1]	94.79[1]	-23.80[1]	-17.10[1]	20.56	22.50[1]
**ASAM *P.deltoides clone*	25.98	97.8	-77.75	-25.14	13.59	36.56
**ASAM *Robinia pseudoacacia L.*	24.98	92.67	-45.78	-28.21	25.61	26.36
**ASAM *Pinus pinaster*	19.81	99.71	-60.25	-23.82	5.14	28.64

*Control ASAM; ** ASAM with Rumex extract; [1] (Mertoglu-Elmas and Sonmez, 2011)

Robinia pseudoacacia ASAM with *Rumex* extract handsheets had been lowest of the two pulping processes.

Likewise, tear resistance is another important feature. Paper used in packaging and printing works must be tear resistant over machinery, calendar, reeling and rotating printing machinery. Besides, tear resistance is the foremost important feature in cement packaging and industrial bags, which must be extremely resistant to tear, paper bags, cardboard boxes and everyday used cardboard handbags (Eroglu, 1985).

Tear index of ASAM handsheets was found higher (6.7 mNm^2 g^{-1}) in *Pinus pinaster* and least (2.8 mN m^2 g^{-1}) in *Robinia pseudoacacia.* ASAM with *Rumex* extract handsheets was also determined higher (5.6 mN m^2 g^{-1}) in *Pinus pinaster* and least (2.3 mN m^2 g^{-1}) in *Robinia pseudoacacia* (Table 2). When ASAM with *Rumex* extract handsheets was compared to the ASAM ones, *Pinus pinaster* ASAM handsheets were highest and *Robinia pseudoacacia* ASAM with *Rumex* extract handsheets were lowest.

Due to its simple application, bursting test is the most widely applied testing procedure in routine factory checks for measuring the consistency to specifications (Casey, 1960).

Bursting index of ASAM handsheets was found higher (6.8 kPa m^2 g^{-1}) in *Pinus pinaster* and least (2.5 kPa m^2 g^{-1}) in *Robinia pseudoacacia* ASAM with *Rumex* extract handsheets was also determined as maximum (5.3 kPa m^2 g^{-1}) in *Pinus pinaster* and lesser (1.6 kPa m^2 g^{-1}) in *Robinia pseudoacacia* (Table 2). When ASAM with *Rumex crispus* extract handsheets were compared to the ASAM ones, *Pinus pinaster* ASAM handsheets were highest and *Robinia pseudoacacia* ASAM with *Rumex* extract handsheets were minimum of them.

Brightness, which relates to high optical smoothness, is an important quality indicator in paper and cardboard (Casey, 1960; Vaarasalo, 1999). Brightness of ASAM handsheets was found higher (45.89 %) in *P.deltoides* clone and lower (31.47 %) in *Pinus pinaster* wood of ASAM process (Mertoglu-Elmas and Sonmez, 2011) . ASAM with *Rumex* extract handsheets were also determined highest (25.98 %) in *P.deltoides* clone and least (19.81 %) in *Pinus pinaster* of ASAM with *Rumex* extract process (Table 3). When brightness of ASAM with *Rumex* extract handsheets was compared to the ASAM ones, *P.deltoides* clone ASAM handsheets were highest and *Pinus pinaster* ASAM with *Rumex* extract handsheets were lowest.

Opacity is an optical paper feature, which is defined by the total amount of light, diffused and non-diffused, passing through (Vaarasalo, 1999: Casey, 1960). Opacity in printing is as important printing parameter affecting the paper quality.

Opacity of ASAM handsheets was found higher (96.92 %) in *P.deltoides* clone and lower (93.46 %) in *Pinus pinaster* of ASAM process (Mertoglu-Elmas and Sonmez, 2011). ASAM with *Rumex* handsheets was also found higher (99.71 %) in *Pinus pinaster* and lower (92.67 %) in *Robinia pseudoacacia* of ASAM with *Rumex* extract process. When opacity of ASAM with *Rumex* extract handsheets were compared to the ASAM ones, *Pinus pinaster* ASAM with *Rumex* extract handsheets were higher, and *Robinia* *pseudoacacia* ASAM with *Rumex* extract handsheets were the lower of the two pulping process (Table 3).

Whiteness on the other hand is another important feature for many varieties of papers. Based upon the whiteness degree, application range of paper and cardboard varies. Whiteness of ASAM handsheets was found higher (W; -7.30 T; -11.10) in *P.deltoides* clone and lower (W;-61.0 T;-20.20) % in *Pinus pinaster* wood of ASAM process (Mertoglu-Elmas and Sonmez, 2011). ASAM with *Rumex* extract handsheets was also higher (W;-45.78 T; -28.21) in *Robinia pseudoacacia* and lower (W; -77.75 T; -25.14) in *P.deltoides clone* of ASAM with *Rumex* extract process (Table 3). When whiteness of ASAM with *Rumex* extract handsheets was compared to the ASAM ones, *P.deltoides* clone ASAM handsheets were higher and *P.deltoides* clone ASAM with *Rumex* extract handsheets were lower of the two pulping processes.

Transparency is determined with the amount of passing non-diffused light. Semi transparency is the limited amount of light passing through the object. Transparency's upper and lower limits are defined with complete opaqueness and complete transparentness. Majority of the commercial papers are semi-transparent (Casey, 1960)

Transparency of ASAM handsheets was found higher (22.78 %) in *Pinus pinaster* wood and lowest (14.41 %) in *P.deltoides* clone wood of ASAM process. ASAM with *Rumex* extract handsheets were also maximum (25.61 %) in *Robinia pseudoacacia* wood and minimum (5.14 %) *in Pinus pinaster* (Table 3). When transparency of ASAM with *Rumex* extract handsheets was compared to the control ASAM ones, *Robinia pseudoacacia* ASAM with *Rumex* extract handsheets were higher and *Pinus pinaster* ASAM with *Rumex* extract were the lower of two pulping process.

Yellowness is one of the important index for colored special paper. Yellowness of ASAM handsheets was higher (33.70 %) in *Pinus pinaster* and lower (21.30 %) in *P.deltoides* clone of ASAM process (Mertoglu-Elmas and Sonmez, 2011). ASAM with *Rumex* extract handsheets was also higher (36.56 %) in *P.deltoides* clone and lower (26.36 %) in *Robinia pseudoacacia* of ASAM with *Rumex* extract process (Table 3). When yellowness of ASAM with *Rumex* extract handsheets was compared to the control ASAM ones, *P.deltoides* clone ASAM with *Rumex* handsheets yellowness was higher and *P.deltoides* clone ASAM was lower, this is a desired property of quality for special paper than the control ASAM ones.

The following conclusions may be drawn from the above results and discussion: The optic properties of ASAM with *Rumex* extract handsheets had higher opacity and yellowness except brightness, whiteness, than those of control ASAM ones, but the physical properties were lower.

It can be suggested that the naturally colored special paper which is made from ASAM with Rumex extract pulp's usage would be appropriate. This paper is very important for the packaging industry because it is made of Rumex extract which is used as antraquinone and dye, instead of synthetic dye. So it is necessary requirement for environmentally friendly organic processes usage.

Acknowledgment

This work was supported by the Research Fund of Istanbul, University Project Number: 1556/16012006.

References

Anonymous: Tappi test methods, 1992–1993. Atlanta, GA, USA. *Tappi Press* (1992).

Baskan, S., A. Davut-Ozdemir, K. Gunaydin and B. Erim-Berker: Analysis of anthraquinone in *Rumex crispus* L. by micellar electrokinetic chromatography. *Talanta*, **71**, 747-750 (2007).

Black, N.P.: ASAM alkaline sulfite pulping process shows potential for large-scale application. *J. Tappi*, **74**, p. 87 (1991).

Casey, J.P.: Pulp and paper chemistry and chemical technology. Second edition,**VIII**, *Interscience Publishers Inc*, pp. 1117-1119 (1960).

Davis, P.H.: Flora of Turkey and the Aegean islands. *Edinburgh Univ. Press, Edinburgh*, **2**, pp. 289 (1965-1985).

Eroglu, H.: Paper and paperboard production technology (Kagit ve karton üretim teknolojisi). Karadeniz Technical Univ., *Trabzon,* Turkey, **90**, p. 602 (1985).

Gullichsen, J.: Chemical pulping. In: Fiber line operations (Eds.: J. Gullichsen and H. C. J. Fogelholm) Book 6A Published by Fabet Oy., Helsinki, Finland, A19 (2000).

Mertoglu-Elmas, G. and S. Sonmez: Print ability properties of some alkaline sulfite-antraquinone methanol handsheets. *Asian J. Chem*., **23**, 2515-2519 (2011).

Patt, R., M. Zimmermann, O. Kordsachia and J.F Hinck: Optimization of the prehydrolysis and pulping steps in ASAM dissolving pulp production. Tappi proceedings; Pulping Conference, 141-146 (1994).

Patt, R., O. Kordsachia and H.L. Schubert : Environmentally friendly technologies for the pulp and paper industry. In: ASAM (Eds.: R. A. Young and M. Akhtar). *John Wiley Sons Inc.,* US, p. 101-132 (1998).

Shatalov, A. A. and H. Pereira: *Arundo donax* L. reed: New perspectives for pulping and bleaching-organosolv delignification. *Tappi Peer-Reviwed Paper*, **84**, 1-14 (2001).

Stockburger, P.: An overview of near-commercial and commercial solvent based pulping processes. *J. Tappi,* **76**, 71-72 (1993).

Vaarasalo, J.: Pulp and paper testing. In: Optical properties of paper (Eds.: J.E. Levlin and L.Söderjhjelm). Published by Fabet Oy. pp. 174-176 (1999).

Yaltirik, F. and A. Efe: Systematics of herbaceous plants (Otsu bitkiler sistematigi). *Istanbul Univ.,* **3568**, 180 (1989).

Zimmermann, M., R. Patt and O. Kordsachia : ASAM pulping of Douglas-fir followed by a chlorine-free bleaching sequence. *J.Tappi*, **74**, 129-134 (1991).