

Preparation of Ion Exchangers from Bagasse by Crosslinking with Epichlorohydrin–NH₄OH or Epichlorohydrin–Imidazole

IVAN ŠIMKOVIĆ,¹ JOSEPH A. LASZLO²

¹ Institute of Chemistry, Slovak Academy of Sciences, 84238 Bratislava, Slovak Republic

² USDA-ARS, National Center for Agricultural Utilization Research, Biomaterials Processing Research Unit, 1815 N. University St., Peoria, Illinois 61604

Received 29 February 1996; accepted 25 November 1996

ABSTRACT: Sugar cane bagasse was crosslinked with epichlorohydrin in the presence of NH₄OH or imidazole. The obtained water-insoluble products were characterized in terms of yield, anion-exchange capacity, packed volume, and dye-binding properties. Yields were highest using a 3 : 1 epichlorohydrin to NH₄OH molar ratio, producing weak anion exchangers. The weak anion exchangers had low dye-binding capacities compared to their total anion-exchange capacities. A 2 : 1 epichlorohydrin-to-imidazole molar ratio proved best for making strong anion exchangers from bagasse. The strong anion exchangers had dye-binding capacities comparable to their anion-exchange capacities, indicating that they might be useful for removing anionic dyes from wastewater. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2561–2566, 1997

Key words: lignocellulose; chemical modification; anion exchange; crosslinking; dye binding

INTRODUCTION

Agricultural residues represent a cheap and environmentally safe source of material for the preparation of ion exchangers that may be useful for metals and color removal from water.^{1–3} To ensure good performance, these materials should be structurally stable under mildly acidic or basic aqueous conditions (pH 2–12). Epichlorohydrin (E), a commonly used crosslinking agent, effectively stabilizes agricultural residues for the preparation of weakly acidic cation exchangers.² The potential for using chemically modified lignocellu-

losic for anionic dye binding has not been fully explored.³ While quaternized cellulose has the ability to bind anionic dyes,⁴ it costs much more than quaternized crop residues, which may also be useful for preparing paper additives.^{5–7} The reaction of E with ammonia in the presence of cellulose produces a weakly basic anion-exchange material.^{8–11} The formation of polyamines by reaction of ammonia with E is well understood ion-exchange polymer chemistry.^{12,13} Thus, there is a body of evidence that suggests that inexpensive dye adsorbents could be prepared from crop residues with reactions involving E and ammonia or other nitrogen-containing molecules.

The present study describes the crosslinking of sugar cane bagasse (B) with E in the presence of NH₄OH or imidazole (I). The obtained weakly and strongly basic ion exchangers were compared according to their total exchange capacity (*Q*) and dye-binding properties. The purpose of this work

Correspondence to: J. A. Laszlo.

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of other that may also be suitable.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/132561-06

was to identify reaction conditions that produce modified bagasse products in high yield having substantial dye-binding capacity.

EXPERIMENTAL

Materials

Bagasse was prepared as described previously.¹ Dyes used were Alizarin Red S monohydrate (Aldrich, dye content 70%; abbreviation: ARS) and Remazol Brilliant Red F3B (C.I. Reactive Red 180, Hoechst Celanese Corp.; abbreviation: F3B) hydrolyzed as described previously.⁴ For some experiments, hydrolyzed F3B was prepared by heating 0.5 mmol of reactive dye (96% purity) at 50°C for 1 h in 100 mL of 25 mM NaOH. The dye was then diluted to a final concentration of 1.0 mM. All other chemicals used were reagent grade.

Methods

Plastic reactors (120 mL volume) with pressure-releasing adapters (pressure up to 830 kPa) or glass vessels equipped with reflux condensers were used for chemical-modification experiments. For the determination of exchanger packed volumes (PV), samples (0.1–0.2 g of sample in Cl⁻ form) were mixed with 10 mL of 0.0975 N NaOH and rotated overnight, centrifuged at 2000 *g* for 10 min in volume-calibrated tubes, and then equilibrated for 2 h. Potentiometric titrations were conducted using a Metrohm 702 SM Titrino (Brinkman) automatic titrator. Following PV determination, the sample solution was then back-titrated with 0.0974 N HCl to determine total exchange capacity (*Q*), using 60 s equilibrium intervals between 0.05 mL additions of titrant (the “excess-NaOH” titration method). For direct titration of the ion-exchanger samples, 1 min to 1 h equilibrium intervals were used. Nitrogen content was determined by the micro-Kjeldahl procedure or with a Fisons EA-1108 instrument.

Dye-binding capacities were determined as a function of solution pH with approximately 15 mg (ARS) or 50 mg (F3B) of exchanger equilibrated for 20 h with 1.0 mM dye solution (100 mL), adjusted to pH 3–11 with solid NaOH or 2 N HCl. At the end of the equilibration period, solution pH was determined and an aliquot was filtered and diluted 50-fold into 100 mM Na₂CO₃ buffer (pH 11.6) to spectrophotometrically determine the concentration of free dye (i.e., dye not bound to

the exchanger).⁴ The amount of dye bound by the exchanger was calculated from the difference between initial and final (equilibrated) dye concentrations.

Chemical Modifications

Bagasse (5 g dry weight) was mixed with 50 g of 17.5% NaOH and stirred at 60°C for 20 min. Subsequently, E (50 g) and NH₄OH (50 g of a 28% solution) were added and the sample maintained at 60°C under reflux for 4 h. The insoluble product was collected by vacuum filtration, washed with water until the filtrate pH was neutral, and then freeze-dried and mechanically homogenized. In this way, B–E–NH₄OH (BEA, *N* = 7.92%, Table I, sample 1) was prepared. Variations on these reaction conditions (i.e., with different ratios of E, NH₄OH, NaOH, and H₂O) are listed in Table I.

Bagasse modified with E and I (BEI) was prepared by reacting B (2 g) with water, E, I, and NaOH, in quantities listed in Table II, in a glass vessel under reflux or in a closed, pressure-releasing plastic reactor for 24 h at 22°C. The obtained BEI samples were washed with deionized water, dried *in vacuo* at 22°C, and homogenized.

RESULTS AND DISCUSSION

A variety of reaction conditions and reactant stoichiometries were examined to determine the influence of these factors on product yield, efficiency of reactant use, and certain physical properties (PV and *Q*) of the prepared exchangers. Reaction efficiency, measured by the yield of the water-insoluble product mass and nitrogen content, determines to a large extent the overall economics of producing these materials. Thus, optimal reaction conditions were sought. Similarly, product total exchange capacity (a function of nitrogen content) was measured since it should reflect the potential performance of the exchanger (i.e., high exchange capacity is preferable to low exchange capacity in most applications). Packed volume reflects the extent of polymer crosslinking in the exchanger, counterbalancing the swelling effect of introduced exchange sites. Large PV values facilitate penetration of ions to exchange sites, but may make the exchanger unsuitable for packed-bed applications.

Table I Results of Crosslinking of Bagasse with E in the Presence of NH₄OH

Sample No.	Bagasse Mass (g)	Moles of Components				Mass Yield ^a (%)	Nitrogen Yield ^b (%)	PV (mL/g)	Q (mmol/g)
		E	NH ₄ OH	NaOH	H ₂ O				
1 ^c	5	0.540	0.370	0.218	3.891	703	44	3.1	4.6
2 ^c	5	0.108	0.286	0.250	1.428	102	6	9.6	3.1
3 ^d	5	0.108	0.286	0.250	1.428	143	9	7.6	3.6
4 ^d	5	0.100	0.033	0.100	0.165	153	77	6.8	3.3
5 ^d	5	0.100	0.300	0.300	1.500	77	2	7.3	1.9
6 ^d	5	0.100	0.100	0.100	0.500	149	34	8.4	4.5
7 ^d	5	0.002	0.002	0.100	0.100	94	38	9.8	1.6
8 ^d	1	0.020	0.020	0.100	0.100	150	28	8.6	3.7
9 ^d	1	0.100	0.100	0	0.500	455	30	7.7	6.6
10 ^d	1	0.033	0.100	0	0.500	75	1	18.0	0.8
11 ^d	1	0.300	0.100	0	0.500	1035	71	4.3	6.9

^a Yield of dry, water-insoluble material as a percentage of initial bagasse weight.

^b Percentage of applied *N* incorporated into water-insoluble product.

^c Stirred in glassware under reflux.

^d Stirred in plastic reactor with pressure-releasing adapter.

BEA Yield and Physical Properties

Large differences in yield, *Q*, and PV of exchangers were observed with modification of B by E and NH₄OH under various reaction conditions (Table I). With very high ratios of reactants to bagasse, product yields and *Q* values were large (samples 1 and 11). The PV values of these products were lower than those of unmodified bagasse (5.4 mL/g). Decreasing the reaction content of

E and NH₄OH lowered yields and increased PV values (samples 2–10). Reaction under closed-vessel conditions (Table I, sample 3) improved yield and *Q* values in comparison to reflux conditions (sample 2). With a closed reactor, pressure was built up during the first few minutes as a result of the exothermic reaction. Under reflux, the reaction remained at atmospheric pressure, which may account for the differences in yields (mass and nitrogen) and *Q* values observed for

Table II Conditions and Results of BEI Experiments

Sample No.	Bagasse Mass (g)	Moles of Components				Mass Yield ^a (%)	Nitrogen Yield ^b (%)	PV (mL/g)	Q (mmol/g)
		E	I	NaOH	H ₂ O				
1 ^c	2	0.008	0.008	0.025	0.333	68	17	—	1.0
2 ^c	2	0.042	0.042	0.125	0.333	93	5	14.1	1.1
3 ^c	2	0.042	0.042	0.125	1.444	70	5	—	1.5
4 ^c	2	0.100	0.100	0.100	0.333	69	2	13.2	1.1
5 ^d	2	0.042	0.042	0.125	0.556	64	2	13.2	0.8
6 ^d	2	0.042	0.042	0	0.556	86	6	14.8	1.5
7 ^e	2	0.100	0.100	0.100	0.333	203	13	9.2	3.1
8 ^e	2	0.200	0.100	0.100	0.333	139	1	10.9	1.2
9 ^e	2	0.100	0.050	0.100	0.300	381	26	7.3	1.7
10 ^e	2	0.020	0.010	0.100	0.500	115	30	8.4	1.3
11 ^e	2	0.020	0.010	0.100	1.000	58	7	8.9	0.6

^a Yield of dry, water-insoluble material as a percentage of initial bagasse weight.

^b Percentage of applied *N* incorporated into water-insoluble product.

^c Stirred in glassware under reflux.

^d Prepared under vacuum (24 h at 22°C).

^e Stirred in plastic reactor with pressure-releasing adapter.

samples generated in closed vs. open reaction vessels.

A 3 : 1 molar ratio of E to NH_4OH (Table I, samples 4 and 11) resulted in the highest NH_4OH incorporation efficiency of the reaction conditions examined. This 3 : 1 ratio suggests that tertiary amines (i.e., three 2-hydroxypropyl groups) are the preferred form of the exchange site created in the insoluble product. Reversing the E to NH_4OH ratio to 1 : 3 drastically decreased yields (samples 5 and 10), implying that mostly soluble polymers are formed under these conditions and are not incorporated into B. With 1 : 1 ratios of E to NH_4OH (samples 6–8), results intermediate to those obtained with 3 : 1 and 1 : 3 ratios were produced. Regardless of the reactant molar ratio employed, potentiometric titrations of BEA samples directly from the free base form showed single endpoints close to pH 4.0, which indicates that only weak amine-exchange sites were produced.

Omitting NaOH from the reaction mixture (Table I, samples 9–11) did not significantly alter the outcome from those reactions containing NaOH with comparable amounts of E and NH_4OH . The absence of NaOH likely precludes the activation of carbohydrate or lignin hydroxyl groups required for reaction with E. Thus, it is likely that samples generated without NaOH present consisted of large polyamine blocks with few or no crosslinks to B.

The percentage of nitrogen in samples, in general, was within 5% agreement with Q values determined by the excess-NaOH titration method. Samples in H^+ form titrated directly with NaOH or samples in free base and/or OH^- form titrated directly with HCl had Q values that were lower than expected based on nitrogen content. This might be due to the inability of the ions to penetrate into the cell wall material within the allowed titrant equilibration time (up to 1 h equilibrium intervals during the titration). It might be also due to the irreversible collapse of the pores caused by drying, as has been hypothesized by others.¹⁴

BEI Yield and Physical Properties

Crosslinking of B with E and I introduces imidazolium groups into the lignocellulosic material. The yields and Q values of BEI derivatives were smaller in general (Table II) than those of the BEA products; conversely, the PV values were larger, indicating a lower crosslinking density. The BEI derivatives, unlike the BEA derivatives, are still charged under the strongly alkaline PV

determination conditions (see below). Charge-induced swelling of the BEI exchangers may account for their generally higher PV values.

Use of a closed reactor again resulted in increased yield and Q values and decreased PV values compared to the reflux reactor (compare samples 4 and 7), which, in turn, was preferable to partial vacuum conditions (compare samples 3 and 5). This suggests that volatile reactants (such as epichlorohydrin) may have been lost in the open systems during the initial exothermic phase of the reaction. Alternatively, pressure buildup in closed reactor may have improved contact of E and I with B polymers.

The extent of I incorporated into B under closed reactor conditions (Table II, samples 7–11) was found to be quite sensitive to reactant ratios. Nitrogen yield (i.e., percentage incorporation of I) was highest with an E : I : NaOH : H_2O molar ratio of 0.02 : 0.01 : 0.1 : 0.5 on 2 g of B (sample 10). Therefore, a 2 : 1 E to I ratio would appear to be best for the efficient use of I. However, the largest BEI Q value was obtained at a 1 : 1 E to I ratio (sample 7). An increase in E to I of 1 : 1 to 2 : 1 without a concomitant increase in NaOH drastically decreased I incorporation (compare samples 7 and 8). Even a modest increase in H_2O in the reaction (0.5 vs. 1.0 mol) diminished yield significantly (compare samples 10 and 11). With such exquisite sensitivity to reaction conditions, it is likely that the optimal BEI synthesis was not achieved in this study.

Direct titrations of BEI samples in OH^- form with HCl displayed a single endpoint, near pH 7.6, reflecting the presence of only imidazolium groups (i.e., strong anion-exchange sites). The absence of additional endpoints in the BEI sample titrations indicates that there were no tertiary amines present as a result of incomplete modification of I with E.

BEA and BEI Dye-binding Properties

The dye-binding capacities of the prepared exchangers were examined as a function of pH (Fig. 1). BEI ($Q = 3.1$ mmol/g, Table II, sample 7) bound more ARS and F3B than did BEA ($Q = 4.6$ mmol/g, Table I, sample 1) over the entire pH 3–11 range. Unmodified bagasse had very little dye-binding capacity. The greater dye binding by BEI, although having a smaller Q value than that of BEA, might be due to a greater affinity of dye for strongly basic imidazolium groups in comparison to the weakly basic BEA exchange sites.

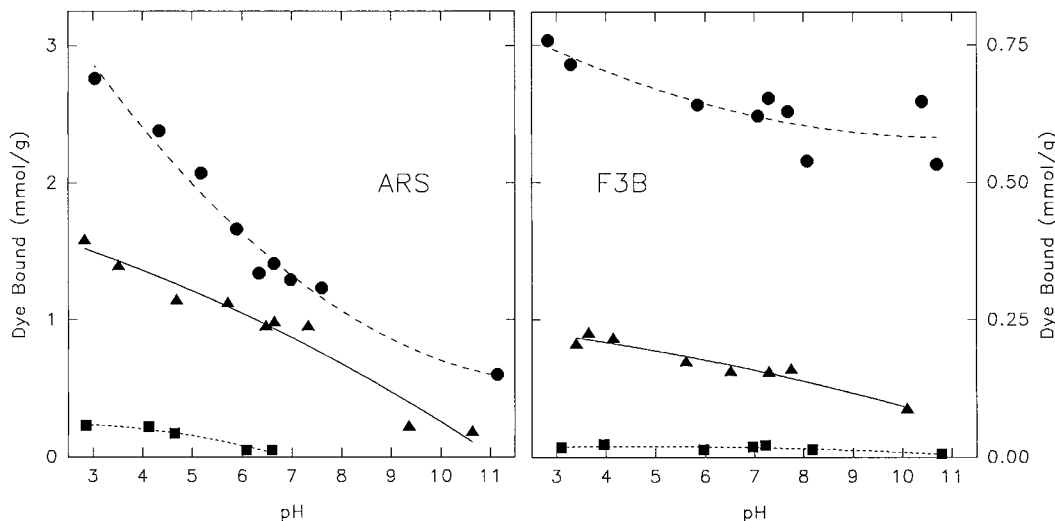


Figure 1 Relation between dye-binding capacity and pH of bagasse samples: BEA (Table I, sample 1; triangle), BEI (Table II, sample 7; circle), and unmodified B (square).

Table III provides a comparison of the dye-binding capacities, determined at pH 3.0, to the total exchange capacity (Q) of selected samples. With BEI, ARS bound to a greater extent than expected based on the total exchange capacity of the sample, while F3B binding was less than Q . The cause of the excess ARS binding is not known, but may result from dye aggregation or stacking on the exchanger similar to that which has been observed with certain water-soluble cationic polyelectrolytes.¹⁵ All the exchangers demonstrated an approximately 3 : 1 molar ratio of ARS : F3B binding ratio, which likely reflects the dyes' 1 : 3 charge ratio at pH 3.0.

CONCLUSIONS

Weakly and strongly basic ion exchangers can be prepared from bagasse by crosslinking with E-NH₄OH or E-imidazole, respectively. For the production of weakly basic resins (BEA), the optimal molar E : NH₄OH : NaOH reactants' ratio is approximately 0.1 : 0.033 : 0.1 (for 5 g of B). For the preparation of the strongly basic anion exchanger (BEI), the molar ratio of E : I : NaOH : H₂O experimentally observed at 0.02 : 0.01 : 0.1 : 0.5 (on 2 g of B) reacted in a closed reactor provided the best conditions for incorporating imidazole into insoluble products. Because the dye-

Table III Comparison of Dye-Binding Capacities and Q Values of Selected Exchangers

Exchanger Type	Sample/ Table No.	Dye-binding Capacity ^a		Q (mmol/g)
		ARS (mmol/g)	F3B (mmol/g)	
BEA	10/I	1.9	0.6	3.8
BEA	8/I	0.5	0.2	3.1
BEA	7/I	0.6	0.3	3.2
BEA	3/I	2.2	0.6	4.6
BEA	4/I	1.0	0.2	3.5
BEI	8/II	2.1	0.6	1.2
BEI	9/II	3.3	1.1	1.7

^a Conditions: All samples were equilibrated with ARS (3 mM initial concentration) or F3B (1 mM initial concentration), at pH 3.0, for 20 h at room temperature.

binding capacities of the BEA exchangers are substantially less than their total exchange capacities, it is unlikely that they would be useful for removing dye from wastewater. The strong anion exchanger BEI products may be quite useful for decolorizing wastewater.

We thank Mary M. Hallengren, Dr. Jacob Lehrfeld, and Helena Lestanska for their advice and assistance.

REFERENCES

1. J. A. Laszlo, *Text. Chem. Color.*, **28**, 13–17 (1996).
2. J. A. Laszlo and F. R. Dintzis, *J. Appl. Polym. Sci.*, **52**, 531–538 (1994).
3. J. A. Laszlo, *Am. Dyestuff Rep.*, **83**(8), 17–21 (1994).
4. J. A. Laszlo, *Text. Chem. Color.*, **27**, 25–27 (1995).
5. I. Šimkovic, M. Antal, and J. Alföldi, *Carbohydr. Polym.*, **23**, 111–114 (1994).
6. I. Šimkovic, J. Mlynár, and J. Alföldi, *Carbohydr. Polym.*, **17**, 285–288 (1992).
7. I. Šimkovic, J. Mlynár, J. Alföldi, and M. M. Micko, *Holzforschung*, **44**, 113–116 (1990).
8. L. L. Grachev, I. V. Somborskii, and A. F. Chetverikov, Ger. Offen. 1,800,308 (1970); *Chem. Abstr.*, **73**, 67253k (1970).
9. J. B. Mc Kelvey, R. R. Benerito, R. J. Berni, and B. G. Beverly, U.S. Pat. 3,441,609 (1969); *Chem. Abstr.*, **71**, 82607 (1969).
10. J. B. Mc Kelvey, R. R. Benerito, R. J. Berni, and B. G. Burgis, U.S. Pat. 3,351,420 (1967); *Chem. Abstr.*, **68**, 3869e (1967).
11. U.S. Food & Drug Administration, Fed. Regist. 20 Nov. 1981, 46(224), 57032-3; *Chem. Abstr.*, **96**, 33473s (1982).
12. R. L. Albright and P. A. Yarnell, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark and J. I. Kroschwitz, Eds., Wiley, New York, 1987, Vol. 8, pp. 341–393.
13. N. Vorchheimer, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark and J. I. Kroschwitz, Eds., Wiley, New York, 1987, Vol. 11, pp. 489–507.
14. K. R. Morgan, J. A. Hemmingson, R. H. Furneaux, and R. A. Stanley, *Carbohydr. Res.*, **262**, 185–194 (1994).
15. B. Vishalakshi, *J. Polym. Sci. Polym. Chem.*, **33**, 365–371 (1995).