Bioconversion of Barex 210 (an Acrylonitrile Copolymer) Nitrogen for Plant Utilization

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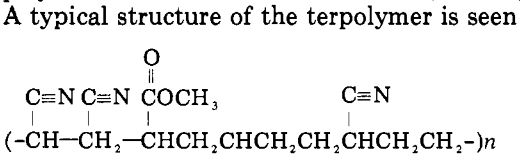
Barex 210 high barrier resin, containing 17% nitrogen, was acid hydrolyzed for 47–50% conversion of the acrylonitrile monomer to the acrylamide form. The treated resin was used as an adjunct in growth substrates to evaluate nitrogen availability for plant uptake. A nitrogen deficient soil was used to demonstrate resin performance as an agricultural fertilizer. Oat seedlings, *Avena*, planted in the soil exhibited dry weight increases over controls in the growth period with increased resin quantities added to the soil. The growth studies showed that hydrolyzed Barex 210 can be used as a source of nitrogen for oats without detrimental effects.

The food packaging industry, especially the carbonated beverage producers, is now interested in the family of high-barrier, break resistant resins for their products. If the packaging materials prove a success, the marketing of disposable containers may be in excess of 80 billion units per year or about 3 million tons of resin (Waechter, Bulletin of Chas. T. Main, Inc.). This will add to already enormous waste disposal problems.

One of the resin producers is Vistron Corporation, a subsidiary of Standard Oil of Ohio. Their resin, Barex 210, is a terpolymer containing acrylonitrile, methylacrylate, and butadiene.

The resin is produced by graft or emulsion copolymerization of 73–77 parts by weight of acrylonitrile and 23–27 parts by weight of methylacrylate in the presence of 8–10 parts by weight of butadiene–acrylonitrile copolymers containing approximately 70% by weight of polymer units derived from butadiene (*Fed. Regist.*, 1970). A typical structure of the terpolymer is seen as follows:



The nitrogen content in the polymer is approximately 17% by weight (Giacin, 1973).

It is desirable to recycle materials after the primary function has been fulfilled and there may be several methods available. One method that may be used without excessive cost and adding other types of pollutants to the environment is to biodegrade the material to another form so that it may have another application.

Because of the unnatural molecular configurations of many synthesized polymers microbial enzymes are often ineffectual in degrading packaging resins. However, if chemical modification can be done to change all or part of the molecular structure so that it resembles a natural polymer it may be possible to achieve partial degradation by enzyme attack at these sites. Work has been done on Barex 210 resin to investigate its disposability by a chemical and bioconversion technique.

Giacin (1973) has found that microbial growth on Barex 210 in nitrogen-deficient media was enhanced by acid hydrolysis of the polymer and that the Barex 210 nitrogen was used for protein synthesis. The removal of Barex 210 nitrogen for microbial utilization indicates that Barex 210 may possibly be used as a source of nitrogen for plants when incorporated into soil. This technique of bioconversion would possibly serve as a means of disposing and, at least, partially recycling these types of high barrier resins.

Planting studies were done using treated Barex 210 plastic as a nitrogen source. The objectives of this research were to determine if treated Barex 210 can supply plants with nitrogen indirectly through microorganisms and the quantity of resin nitrogen made available, by microbes, for plant uptake.

Table I. Soil Characteristics in the Pots of the Soil Growth Study (Experiment 1)

Adjunct label	ppm of N added
Control 1 & 2	0.0
1.41 g of H.B.[a] 1 & 2	100[b]
2.82 g of H.B. 1 & 2	200[b]
5.0 g of H.B. 1 & 2	355[b]
NH_4NO_3, 25 ppm 1 & 2	25
NH_4NO_3, 50 ppm 1 & 2	50
NH_4NO_3, 100 ppm 1 & 2	100

[a] Hydrolyzed Barex 210. [b] Parts per million added in acrylamide form of H.B.

EXPERIMENTAL PROCEDURE

Barex 210 resin was finely ground on a Wiley Mill and 20 g of the powder was placed in a pressure reactor with 40 ml of 5% H_2SO_4. The reactor was held at 180 °C for 2 h with an internal pressure of 80–90 psi. The product was washed thoroughly and ground to a fine powder once more on the Wiley Mill. This process yielded Barex 210 having 47–50% of the acrylonitrile copolymer hydrolyzed to acrylamide (Gilbert, 1974).

The soil used in the experiment had been closely monitored for 8 years by the Soils Department of Rutgers University and was mostly deficient in overall nitrogen content. The Freehold sandy loam soil was analyzed and found to be within normal agricultural ranges for inorganic elements. The pH was 6.3 and the soil contained 12 ppm of nitrate form nitrogen and 4 ppm of ammonium form nitrogen. (A desirable range of nitrogen concentration for good plant growth in soil is between 50 and 100 ppm (Flannery, 1973).)

Fourteen polyvinyl chloride (PVC) pots were placed on aluminum plates in a greenhouse. About 5 cm of washed gravel was placed in the bottom of each pot and 1 kg of dry soil on top. Soil treatments were made in duplicate with the addition of various amounts of NH_4NO_3 and hydrolyzed Barex 210 (Table I). The treated soil was then moistened with distilled water.

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Table II. Approximate Nitrogen Gains of Plant Tops in Experiment 1[a]

Samples (2)	Control	1.41 g of H.B.	2.82 g of H.B.	5.00 g of H.B.	NH_4NO_3, ppm		
					25	50	100
Av dry wt	340	630	810	1157	743	917	1357
per plant top, mg[b]	470	580	770	1157	733	960	1187
% N[b]	1.3	1.4	1.5	1.5	1.4	1.6	1.7
	1.2	1.3	1.7	1.4	1.4	1.3	2.2
Av amt of	4.4	8.8	12.2	17.4	10.4	14.7	23.1
N in dry plant top, mg[b]	5.6	7.5	13.1	16.2	10.3	12.5	26.1
Approx. N gain	4.1	8.5	11.9	17.1	10.1	14.4	22.8
per top in growth period	5.3	7.2	12.8	15.9	10.0	12.2	25.8

[a] Average dry weight per plant seedling (experiment start) = 5.4 mg. Average percent N (experiment start) = 5.3. Average amount of N in 1 dry seedling (experiment start) = 0.3 mg. [b] Post harvest.

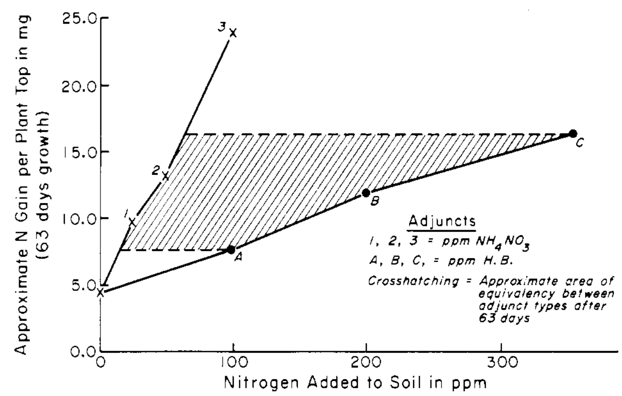

Figure 1. Average N gain per plant top vs. concentration of soil adjunct in experiment 1.

The pots were incubated in the greenhouse for 1 week while oat seedlings (*Avena*) were growing, in a sand germination flat, also for the same period of time. At 1 week's time, three seedlings were transplanted into each of the 14 pots. The seedlings were planted so that the tip of the coleoptile was close to the surface of the soil.

The plants were allowed to grow for a period of 62 days (12/12/73 to 2/13/74), and during that period of time observations of growth and the height of all the plants were recorded about every 3 days. The soil was kept moist by alternately watering the pots from the bottom and from the top to counteract leaching of the nutrients.

At the end of the growth period the oat plant tops were harvested, by cutting at the soil surface, and the wet weight, dry weight, and moisture content of the plants were determined. The plants were chopped up and dried in a hot air drier for 6 h at 65 °C. Then the nitrogen content of the plants was determined by the micro-Kjeldahl technique (AOAC, 1970).

RESULTS AND DISCUSSION

The final height values taken for the soil growth study showed that increased amounts of resin adjunct in the soil from 1.41 to 5.00 g increased the amount of plant growth. Increased concentrations of NH_4NO_3 also produced greater growth responses. An amount of 100 ppm of hydrolyzed resin nitrogen produced a lesser growth response than an equivalent quantity of inorganic nitrogen added to the soil.

The dry weight increase over the control with the addition of hydrolyzed Barex 210 seems substantial (see Table II). Growth of oats attributed to the 5.00 g of Barex 210 adjunct appears to be equivalent to growth of plants in soil having between 50 and 100 ppm of NH_4NO_3 nitrogen. This assumption is made by the comparison of dry weights of plants from pots with these adjuncts.

The mean plant heights over the growth period were used to compare both adjunct types. The average mean heights for 0.0 g (control), 1.41 g of H.B., 2.82 g of H.B., and 25 ppm of NH_4NO_3 were all significantly less than the average mean heights of plants grown on 100 ppm of NH_4NO_3 nitrogen. It was seen that the mean plant height at 355 ppm of hydrolyzed Barex nitrogen compared closely to the mean height produced by 50 ppm of NH_4NO_3 nitrogen. The data show less nitrogen availability from Barex 210 compared to the inorganic nitrogen source.

In Figure 1 the values for nitrogen gains from Table II were plotted against the concentration of the soil adjunct. The crosshatched area shows the approximate area of equivalency between hydrolyzed Barex 210 and NH_4NO_3, in experiment 1.

Since the addition of 355 ppm of organic nitrogen or 5.00 g of hydrolyzed Barex 210 in 1 kg of soil produced growth comparable to the addition of 50–100 ppm of NH_4NO_3 nitrogen, the concentration seems adequate to fortify nitrogen-deficient soil for good crop growth. However, with a longer incubation period less hydrolyzed Barex 210 may be needed to supply adequate nitrogen for plant uptake.

CONCLUSIONS

Viewing the plant growth data from experiment 1 it may be necessary to use approximately 7.1 times as much Barex 210 nitrogen in the amide form to produce similar growth responses from NH_4NO_3 in soil over a 2-month growth period.

This study showed that hydrolyzed Barex 210 can be used as a source of nitrogen for oats without detrimental effects. The best application of the resin would possibly be as a slow release fertilizer because bioconversion postpones resin nitrogen availability. This lag time makes use of Barex 210 as the sole nitrogenous fertilizer undesirable with crops requiring much nitrogen in a short time period.

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