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Recovery of Chemicals from Agricultural Residues— A Critical Review

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The present trend in increased agricultural products has made the disposal of agricultural wastes a chronic problem. Effective utilization of these wastes will give rise to a large number of useful byproducts. Proper utilization of agrowastes can offer immense opportunities in improving the economic conditions of the farmers and create new employment avenues among the rural masses. Further, this will go a long way in reducing environmental pollution in the countryside. This paper reviews a few important treatments of most of the frequently encountered agro-residues with a view to recover the chemical wealth present therein.

INTRODUCTION

Agriculture, the essential industry for human existence and the backbone of Indian economy, accounts for the income of over 85 % of its population and employs three-quarter of its working force. Every agricultural product leaves behind a significant quantity of waste which is not being economically utilized. Hence an appropriate step towards economic utilization of agro-residues will not only enhance the energy-starved existence of the country but will also escalate its rural development.

The earlier conceptions of waste as a bulky mass, whose obstructive aboundance is irksome, which is expensive to dispose of and likely to pose serious threat to the environment and the natural ecological system has changed. It is being viewed as a storehouse of many valuable products, ranging from fuels and chemicals to soil-conditioners and proteins.

AGRO-RESIDUES AT A GLANCE'

. Most of the agro-wastes can be grouped into three major categories : (i) cellulosic wastes, (ii) non-cellulosic wastes, and (iii) partially waste chemical-rich agricultural products. These can be further classified as wastes obtained during harvesting and subsequent processing.

Cellulosic wastes constitute mainly straws of paddy, wheat, linseed and *ragi*, corn stover and cobs, bagasse and cotton linters. Of these, straws are obtained essentially during harvesting.

Non-cellulosic wastes consist mainly of products obtained during the processing of agricultural products. These include rice and wheat husk, rice bran, cotton seed flour, cotton seed hull, coconut shell and pith, oil seed cakes, sugarcane filter cake and sludge, etc. There is also the *heap* contributed by tea, tobacco, cashew-nut, sisal, nuxvomica and many other domestic and wild plants, which leave behind their Respective byproducts, *viz* shells, hulls, leaves, seeds, kernels, flowers and fruits. The partially-waste chemical-rich agricultural products consist mainly of *mahua* flowers, cashew apple, artichokes and *arhar* sticks. Fig 1 shows a broad classification of the major agro-wastes.

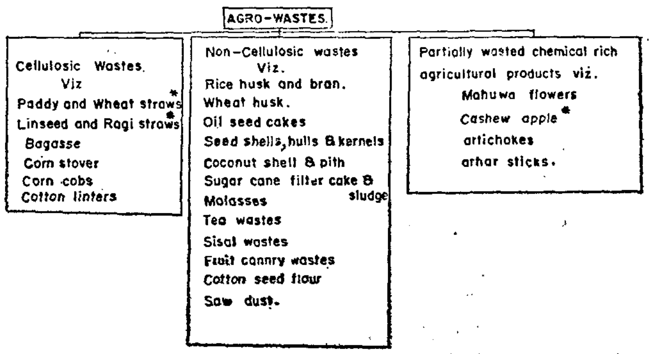

Fig 1 Classification of agro-wastes

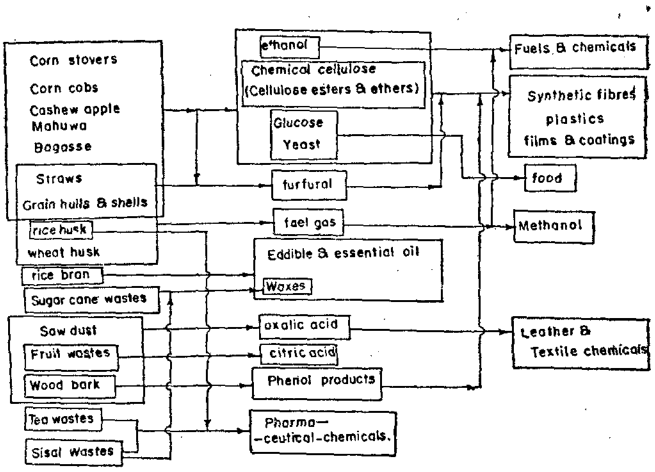

Fig 2 Chemicals from agro-residues and their uses

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POTENTIAL CHEMICAL WEALTH OF AGRO-WASTES

The so-called waste materials are storehouse of various industrial chemicals with diversified uses (Fig 2). Chemical composition of some of the important agro-wastes are given in Table 1. A steady recovery and supply of chemicals from these wastes is a strong point in their favour, as there is no dearth of such raw materials (Table 2).

TABLE 1 COMPOSITION OF SOME IMPORTANT AGRO-WASTES

Agro-waste	Penthosan, %	Hexosan, %	Lignin, %	Cellulose, %
Corn Stover	15.0	35.0	15.0	35.0
Corn Cobs	28.1	36.5	10.4	25.0
Wheat Straw	19.0	39.0	14.4	28.0
Rice Straw	17.0	39.0	10.0	34.0
Oat Hulls	29.5	33.7	13.5	23.3
Bagasse	20.4	41.3	19.9	18.4

TABLE 2 ANNUAL AVAILABILITY OF SOME IMPORTANT AGRO-RESIDUES

Agro-residue	Quantity (million tons)
Rice Husk	20.0
Rice Bran	3.0
Wheat Husk	7.6
Cotton Seed Flour	0.6
Wheat Straw	150.0
Bagasse	4.0
Waste Molasses	0.56
Sugarcane Filter Cake	0.36
Tea Waste	0.01

TREATMENT OF AGRO-WASTES FOR CHEMICAL RECOVERY

TREATMENT OF CELLULOSIC WASTES

Manufacture of chemicals from cellulosic materials will be an additional achievement in productive processes. From the main constituents of cellulosic residues—cellulose, penthosans and lignin—many important compounds can be obtained.

Glucose

Hydrolysis of cellulosic wastes can be carried out to produce glucose. A continuous process for the manufacture of glucose is shown in Fig 3. The product of submerged fermentation by mutant of triehoderma is directly used as the enzyme solution in the hydrolysis vessel. It is observed that 0.5 t of glucose can be produced from every ton of cellulosic waste.

Chemical Intermediates

Furfural : Furfural is an important intermediate which finds extensive use in the manufacture of adipo-

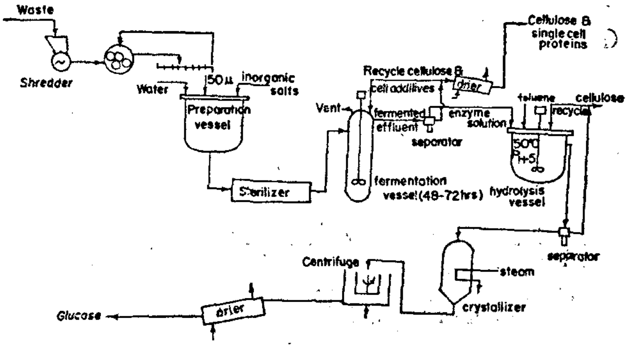

Fig 3 Manufacture of glucose from cellulosic wastes

nitrile, furfural alcohol and resins and in solvent-refining of mineral oils. The contribution of various agro-wastes in the production of furfural in India is given in Table 3.

TABLE 3 MANUFACTURE OF FURFURAL FROM VARIOUS AGRO-WASTES

Agro-wastes	Quantity Produced, %
Rice Bran	2—3
Maize Bran	6—7
Rice Husk	5—6
Paddy Straw	3—4
Bagasse	10—12
Corn Cobs	12—15
Coconut Pith	10—11
Cotton Seed Hulls	17.5
Others	29.1

The process consists of cooking of the ground waste for two hours in rotary steel digesters with a solid-to-liquid ratio of 4:1 followed by separation with the help of azeotropic distillation (Fig 4).

Oxalic Acid : Oxalic acid, an important chemical in ink, leather and textile industries, is obtained from sawdust, wood bark, grain hulls, etc with the help of following manufacturing steps (Fig 5): (1) Fusion with aqueous hydroxide; (2) Leaching, (3) Cooling and crystallization; (4) Causticization; (5) Acid reaction. Data of a typical experimental run is given in Table 4.

TABLE 4 DATA OF A TYPICAL RUN USING SAWDUST

Feed	kg	Product	kg
Sawdust	45.3	Oxalic acid	20.6
NaOH	4.0	Acetic acid	5.3
CaO	15.7	Formic acid	1.1
H_2SO_4	27.7	Methanol	2.5
		$CaSO_4$	38.5
		Wood oils	1.4

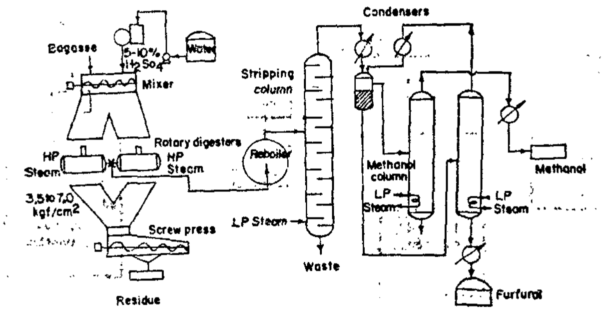

Fig 4 Manufacture of furfural from bagasse

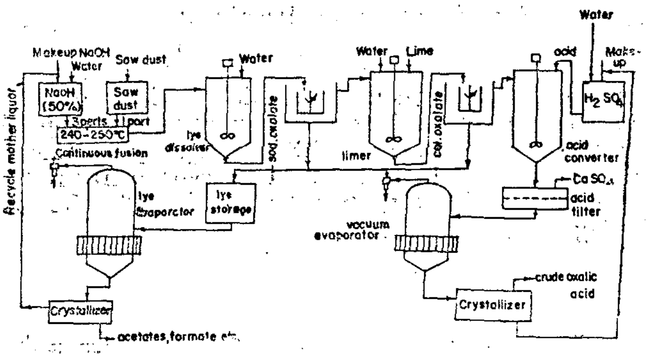

Fig 5 Oxalic acid from sawdust (gay lussac)

Alcohol : The straws and the husks, which are poor sources of energy, can be acid-treated and fermented like molasses.to produce ethanol. Every 20 Mt of waste will yield about 2 Mt of 95 % alcohol. Practically any cellulosic waste can be used to produce alcohol. Further, *mahua* flowers and cashew apple also contain vast amount of fermentable sugars which can be converted to alcohol. The ethanol thus obtained could also be used to produce gasohol, the recently developed substitute for motor fuels.

Chemical Grade Cellulose

Purification of the cellulosic pulp, obtained by the alkali digestion of cellulosic agro-wastes, will yield high purity chemical cellulose useful for synthetic fibre industry. Further, many important chemical compounds can be synthesized by the direct hydrogenation and estefification of these cellulosic residues.

Chemical Fuels

Pyrolysis or thermal decomposition of cellulosic wastes gives rise to a gaseous mixture consisting of methane, hydrogen, carbon monoxide, carbon dioxide and other hydrocarbon gases, which has a calorific value of about 6 200—7 100 kcal/m^3. The oil fraction obtained has a calorific value of 5 500 kcal/kg and the water fraction consists of a variety of chemicals such as aldehydes, acids, ketones, alcohols and phenols. The final residue known as 'char' possesses activation properties.

Other than pyrolysis, the anaerobic digestion of almost any agro-residue, which is carried out at 34°C and neutral pH for one to two weeks, could also yield a gaseous product consisting of methane and having an appreciable calorific value. The methane thus obtained can be used to produce methanol, acetylene, chloromethane, etc which in turn can be used to produce synthetic petrol, chloromethane, formaldehyde, acetic acid, acetone, ethylene, acetaldehyde, etc.

Ethyl alcohol, the process of manufacture of which has been discussed earlier, is another important liquid fuel. Recent developments in using ethanol and also in admixture with gasoline or ether in internal combustion-engines has made it the most important liquid fuel at present.

TREATMENT OF NON-CELLULOSIC WASTES

Rice Husk

Being lignocellulosic, rice husk finds extensive use as raw material in the production of a variety of organic chemicals. It also contains large proportions of silica which forms the basis of a number of inorganic chemicals. Considering its organic chemical wealth, hemicellulose can be converted to xylose from which xylitol, furfural, etc can be obtained. Similarly, cellulose can be converted to glucose arid then to sorbitol or ethanol. Lignosulfonic acids are also obtained from lignin. Table 5 gives the composition of rice husk.

TABLE 5 COMPOSITION OF RICE HUSK

CONSTITUENTS	% BY WEIGHT (ON DRY BASIS)
Ash	20
Hemicellulose	18
Cellulose	38
Lignin	22
Others	2

Chemical conversion of rice husk may be based on the entire organic content (80% on dry basis) or on each constituent of organic matter. Schematic representation of the processing of total rice husk to produce chemicals and fuels is shown in Fig 6.

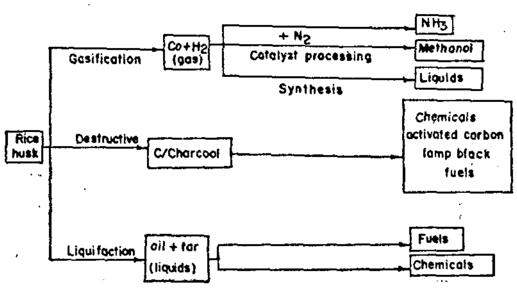

Fig 6 Processing of total rice husk

The primary processing steps are drastic, non-selective and involve high pressure/temperature. These primary products are processed like petroleum fractions. In all these processes, the silicious ash remains as residue which, forms the source of a variety of inorganic chemicals.

Hemicellulose, which constitutes 18% of rice husk, is essentially a glucoxylan. The chemicals produced by its processing are widely used as raw materials, intermediates and solvents in pharmaceuticals, synthetic fibres, fungicides, preservatives, foods, cosmetics and synthetic resins.

Cellulose, which constitutes about 38 % of rice husk, is a higher polymer of glucose. Most of the chemicals obtained from cellulose find use in the fibre industry, plastic and in the manufacture of ethylene and butadiene.

Lignin is the major non-carbohydrate part (22 %) and is a randomly linked polymer of phenyl propane units. This needs severe conditions for chemical conversion. Lignosulfonic acids can be used in the preparation of detergents, vanillin and also for foundry preparations.

Rice husk ash is essentially 95 % silica. Ash as residue from chemical conversion of organic matter appears to be a better source for the conversion to silica-based products than ash by burning, because burning transforms the amorphous form into non-reactive crystobalite form. The residue of rice husk and straw after production of furfural can be utilized to make sodium silicate and in turn silicagel, zeolite, etc and active carbon is obtained as a byproduct. Husk can be directly used to produce silicon carbide and calcium silicide in electric furnaces. This could also be used as an intermediate for the production of nylon 44. Ash can also be admixed with lime or cement to produce strong and at the same time cheap binders.

Rice Bran

After removal of rice husk, when rice is subjected to polishing, rice bran is obtained which averages around 6 % of paddy. The composition of rice bran is given in Table 6.

TABLE 6 COMPOSITION OF RICE BRAN

Constituents	%
Water	8.9—14.7
Protein	10.6—13.4
Fat	10.1—22.4
N-free Extract	38.7—44.3
Fibre	9.6—14.1
Ash	9.3—14.3
Penthosan	8.7—11.4
Cellulose	11.4
Reducing Sugars	1.3
Sucrose	10.5

Since India has to import edible oil to meet the present demand, it would be worth-while to utilize non-conventional sources such as rice bran, for the extraction of edible oil. Rice bran contains 18-20% edible oils and is a potential source of most of the B-complex and group vitamins. At present, if all the rice bran produced is utilized, about 3 Mt of edible oil can be extracted. The wax separated (after extraction of oil) has similar properties of waxes as obtained from any other plant source. Fig 7 shows the important rice bran chemicals and their uses.

Oil extraction from rice bran can be effected by using solvent like hexane, ether and propane at reduced pressures and the concentrated miscellaneous is distilled *to* recover solvent which leaves behind the oil. Oil is stripped of the remaining solvent in a gravel-packed column by open steam. Crude oil contains wax, unsaponifiable matters and other ingredients. The main problem is the high fatty acid content of extracted oil.

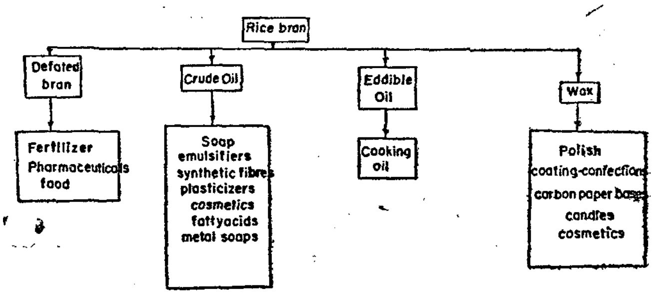

Fig 7 Rice bran chemicals and their uses

Research for eliminating or inactivating the enzymes responsible for the splitting of fats to fatty acids is in progress. However, fresh rice bran is found to yield less fatty acids when extracted. Various refining steps for crude oil include dewaxing by ketones, degumming by concentrated H_3PO_4 or H_2SO_4 treatment, filtration, removal of fatty acid by caustic treatment,, decolorization by earth bleaching and deodourization by high temperature heating.

Sugarcane Wastes

Different treatments of bagasse to produce cellulose and related products such as alcohol, furfural, lignin, etc have already been discussed earlier.

At present, molasses,, which accounts for more than 0.3 Mt of alcohol, can also be used to produce yeast and citric acid. Manufacture of citric acid releases considerable amount of sugar and also helps in reducing import of calcium citrate and citric acid.

The filter cake obtained after filtration of sugarcane juice can be a good source of wax. The precipitated cane juice contains wax that was originally on the surface of the stalk before it was crushed. The cake is mixed with solvents which dissolve the wax as well as other solubles. The solvent is evaporated, recovered and recycled. The residue is waxy containing about 50% sugarcane fatty oils and 20% resinous matter. This crude wax on refining contains about 55% waxy esters, 8% alcohol, 25% ketone and 2% hydrocarbons. This wax has the same properties as any other hard natural wax and can be used in the manufacture of shoe polish, wax and carbon paper. Sugarcane sludge also yields some amount of wax and precipitated calcium carbonate useful for industry.

Tea Wastes

Tea wastes consist of sweepings of the fluff, stalks and leaves. This is a cheap source of caffein, an important raw material for the pharmaceutical industry. To reduce solvent losses and operational hazards, a two-step process is usually practised in the extraction *of* caffein. Caffein is first leached into aqueous phase with water and this aqueous extract is subjected to liquid-liquid extraction using solvents such as benzene, chloroform, ethylene dichloride, etc. A waste-to-water ratio of 1:4 is used, and 33 % of lime is also added to facilitate maximum leaching. Fig 8 gives the different steps in the manufacture of caffein.

The decaffeinated tea-waste offers a valuable source of low melting wax useful in the production of pharmaceuticals and cosmetics. This wax contains about 20% palmitic acid.

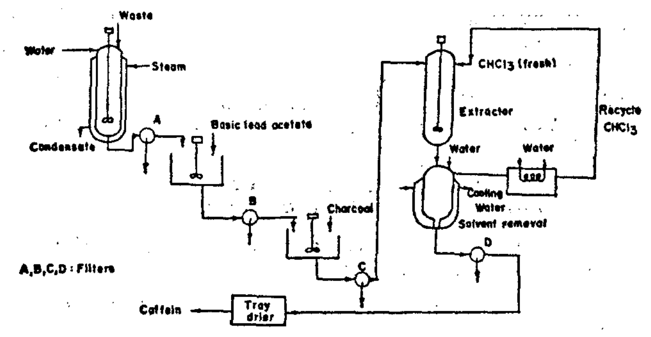

Fig 8 Manufacture of caffein from tea-waste

Sisal Waste

The juice and residue left after removal of sisal fibre can be used to produce wax and lucoyonin, a valuable starting material for the production of certain steroid hormones. The sisal wax could possibly replace the imported carnuba wax.

Fruit Wastes

Pineapple wastes can be used to prepare 'bromelin' which is a proteolytic enzyme and other fruit cannary wastes can be used to prepare oxalic acid. Coconut shell can be used to produce active carbon and charcoal.

Miscellaneous Wastes

Tobacco waste, residue left after extraction of alkaloid from nux vomica and *arhar* sticks, can be used to make oxalic acid in a cheap manner.

TREATMENT OF PARTIALLY WASTE CHEMICAL-RICH AGRICULTURAL PRODUCTS

Cashewnut Apple and Shell-Liquid

Cashewnut apple contains 10.4% fermentable sugars and is used for preparing alcohol by fermentation. The residue after extraction of juice from apple can be used to make oxalic acid, Cashewnut shell liquid, a byproduct of the cashewnut industryj is widely used in the preparation of acid and alkali resistant paints, varnishes and resins. It contains 60-30% of phenols which could be recovered with the simultaneous production of cardanol. It is used in the manufacture of plywood and cation exchange resins.

Mahua Flower

It is a rich source of fermentable sugar and can be used to produce alcohol. Residue left after extraction of sugar can be used to make oxalic acid.

CONCLUSION

It has been observed from earlier discussion that agro-wastes and agro-byproducts, which are rich sources of important industrial chemicals, can meet country's demand to a considerable extent if fully and properly utilized. Recovery process of some of the chemicals on a limited scale have already been established (Table 7).

Moreover, if waste materials are properly utilized, more economic opportunities can be offered by improving the availability of some essential raw materials in addition to maintaining a healthier rural environment. The two most important achievements which could be obtained by the recovery of chemicals from these wastes are its catalytic role in the rural development and the preservation of the ever-depleting fossil fuels such as coal and petroleum.

TABLE 7 . PRODUCTION STATISTICS FOR SOME AGRO-BASED CHEMICALS *

Item	Production (t/yr)		Agro-wastes used	Present demand, t/yr	Quantity produced from wastes, t/yr
	Total	From agrowastes only			
Cellulose Acetate	9 463	—	Conventional raw materials	28 520	—
Chemical Cellulose	5 800	—	Bagasse	19 000	320 000
Glucose	218	—	Bagasse	14 000	672 000
Power Alcohol	163	—	Bagasse, rice bran, maize bran and husks	360 000	160 000
Ether	360	—	-do-	440	660 000
Ethanol	1 25 740	50 000	Mahua flowers	290 000	50 000
Methane	—	—	Animal manure and plant residues	—	1700 000
Oxalic Acid	495	—	Saw dust, cashew apple waste and others	512	500 000
Furfural	6 000	6 000	Bagasse and rice husk	15 000	950 000
Caffein and Salts	66	66	Tea wastes	89	225
Acetic Acid	750	—	Saw dust	57 000	121 000
Vegetable Oil	3 500 000	60 000	Rice bran	4200 000	300 000
Waxes	—	0.4	Sugarcane filter cake	1 000	—
Phenol	8 594	—	Conventional sources	43 000	—

***Source : This information is collected from various journals, seminar proceedings and publications.**

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