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ORGANOSOLV PULPING: A PROMISING PROCESS FOR AGRICULTURAL RESIDUES

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Abstract

This paper reviews the Organosolv pulping process and describes the pulping of agricultural residues, the Rice Straw. The effect of alkali charge in the Alkali-Ethanol system and of cooking time is reported. It is shown that, the pulping of agricultural residues with low lignin content and low basic density can be pulped satisfactorily with Organosolv pulping process. It is indicated that the success of this process depends on development of a suitable recovery process and application of by-products.

Introduction

Organosolv pulping though not a new process has received new attention since seventies, with a steep rise in capital investment requirement for the conventional pulping plants. Increasing awareness of pollution caused by conventional processes has also drawn the attention of technologist's for the development of better processes to minimise environmental impact on pollution. Paper being an essential commodity, the needs of the society all over the world are ever increasing at the rate of 2 to 3 per cent per annum. Raw material utilisation is not only increasing but also, it has diversified covering non-conventional wastes from industry and agriculture. Hence, there is a need for not only processes for conventional raw materials but also for non-conventional ones, which should be techno-economically viable even at smaller scale. Recent developments in Organosolv pulping show that such a process is now possible for the conventional raw materials. However, not much work has been done on the suitability of this process for non-conventional raw materials, more so in our country.

To investigate the suitability of Organosolv pulping for agricultural residues such as straw, work has been taken up as a part of the U.G.C. aided project on 'Organosolv delignification of lignocellulosic materials'. This paper describes the possibilities and experimental findings of pulping of rice straw and indicates suitability of techno-economic viability for a pulping unit on small scale.

An over view of Organosolv pulping

The efficiency and specificity of Organosolv in delignification was recognised in the early part of the century. Further development was hindered due to lack of useful applications of by-products and rapid growth in other processes which were found to be more economical. Though the conventional processes contributed to large scale pollution of the environment, the lack of awareness prevented alternative non-polluting processes. In the later half of the century, increasing pollution gave greater impetus for the prevention of pollution with viable new processes.

The earliest work in this field by Kleinert and Tayenthal studied the action of ethanol on woods in 1931 and showed a strong delignification effect[1]. Later, Arnovosky and Gortner worked using butanol as solvent for delignification of softwood in 1936[2]. The basic principles of bulk delignification were shown by Kleinert et. al to conventional pulping methods as well as for Organosolv pulping in the year 1967[3]. The same authors have found in 1974, aqueous ethanol system in medium concentration and elevated temperature and pressure to be a powerful agent in pulping hardwoods and softwoods[4]. Further claim is made that, this system provides production of good strength pulp at increased yield

and drastic reduction of stream and air pollution. In a study on rate constants and activation energy of ethanol-water delignification of wood, Kleinert T.N., has reported that an activation energy of 28.1 K.Cal/mole for Ethanol-Water pulping which is less than soda (32.0 K.Cal/mole) and kraft (32.2 K.Cal/mole) indicating the higher efficiency of delignification[5].

In mid seventies, Alkaline-Alcohol systems were worked by various people showing promising results. Junzo Nakano et.al. in their studies have shown that alkali-methol cooking system provides one of the pollution free pulping methods. They have found that the rate of delignification was more rapid than in kraft pulping owing to alkylation and prevention of condensation of a - position of lignin giving 7-8 % higher yield due to retention of carbohydrates[6]. The optimum conditions of pulping found to be: cooking liquor containing 40 gms NaOH, 400 gms Methanol per litre. Maximum temperature 160°C. and cooking time 30-60 minutes. A typical yield with cooking at 30 and 60 minutes at the above conditions for Beach wood given are 56.2 and 55.4 % having 4.0 and 1.5 % lignin in wood. In 1980, Katzen and co-workers showed that pulping with ethanol is an economically viable alternative to the conventional processes. They have profounded Alcohol Pulping and Recovery process (APR process) for a hypothetical commercial plant. The plant uses stationary extractors and alcohol recovery system. He has shown the economic viability on the basis of 1979 prices wherein R.O.I. works out to 13 % in case of no recovery of by-products and 22 % with the by-products. It is also claimed that, it is a low pollution pulping process with good profitability[7].

A comparative study of soda and NaOH-Ethanol system made by Marten, R. and Granzow, S., showed that addition of alcohol to NaOH has a synergistic effect on pulping. This is claimed to be more rapid and selective than NaOH alone and yield and brightness of NaOH-Ethanol pulp are improved at a given Kappa No. The fibre liberation point is reached at 55 % yield compared to 50 % for soda pulp. The energy requirement for beating is less and strength and brightness are superior. In their work conditions of pulping given are as under:

1:1 Ethanol-water by volume, with 20 % NaOH on wood basis. Bath ratio 5:1.

In early eighties, a couple of agencies have developed process for Organosolv pulping. A few of them are - ALCELL process (formerly) known as APR process, Alcohol Pulping and Recovery) developed by Repap Technologies, Inc., BEC process, developed by Biological Energy Corporation, Valley Forge, Pennsylvania and the MD process developed by MD Company, Munich, West Germany. However, Organosolv pulping process yet to establish their viability technically and economically much against the proven technologies. But, this holds promise in capital cost advantages, increasing environmental demands and meeting the needs of small scale industries.

Potential Raw Materials

The raw material position in India is altogether different from the major pulp and paper producing countries. Much Research and Technology development is done in countries having large resources of softwoods and to some extent on hardwoods. And any development of process is judged in relation to these raw materials but, non-woody fiberous raw materials which form a bulk of raw materials in third world countries have received little attention towards development of suitable technology. India is endowed with very little of forest resources which is depleting very rapidly. The forest cover is only 22.1% of the total land area forming 0.09 hectare per capita. India being an agricultural country having 46.6 % of agricultural coverage of the total land area, forming 0.24 hectare per capital, offers vast scope for providing non-woody fiberous raw material to meet the increasing demand. With steep rise in capital investment requirement for putting up/operating costs of pulping facilities using these raw materials development of altenative technology has became necessary. Further, raw materials obtained from agricultural sources are widely scattered and also bulky, do not lend practicable large scale centralised pulping facilities.

Therefore, the technology sought after must be technically and economically feasible in small scale with minimum safety hazards so that the pulping units can be located at suitable locations offering other infrastructure facilities. At the present production level in our country about 3 % of forest produce is being used by paper industry and the estimated demand at 2000 A.D. is around 6%. Even with such low percentage of utilisation considerable scarcity of raw material and high level of forest denudation is experienced. The only alternative left is to go for increased use of agricultural residues. As per one estimate, the availability of rice straw and wheat straw together will be around 400 lakh tonnes per annum, after providing for fodder, fuel and other applications to the extent of 80 % of the total availability. Among the other agricultural residues, the availability of Bagasse is estimated to be 40 lakh tonnes per year. Waste from crops such as jute, kenaf, cotton and agave are also considered potential source of raw material.

Organosolv Pulping of Agricultural Residues:

In a recent conference on solvent pulping organised by Doshi & Associates Inc., Appleton, Wisconsin, rounded up the panel discussion, Professor Sarkanen characterised solvent pulping as a 'a new method of a limited promise'. It may be true for the large scale, softwood based pulping units but, detailed study on the suitability of this process on annual crops doesn't seem to have been done.

Solvent pulping is unique by its selectivity of delignification and higher carbohydrate retention both of which are advantageous for agricultural residues which are rich in lower carbohydrates and lower lignin content.

The conventional processes with their severe conditions are found to eat up a greater amount of carbohydrates for a given residual lignin. The low basic densities of these raw materials do not pose the problem of penetration of organic solvents and the unique nature of organic solvents is that, the delignification starts from middle lamella inward and achieves fiber liberation point at a much higher yield level of about 5 to 6% in comparison to conventional alkaline process. The process conditions of temperature and pressure so far studied on softwoods have been quite severe as maintained in conventional processes. In the case of agricultural residues, milder conditions could be effective minimising the hazards associated with high temperatures and pressures. This process also offers easy recovery system and lower pollution impact on environment, which is one of the major considerations of the present time.

Experimental

Rice straw was collected from the local paddy fields. Commercial ethanol was distilled in the range of 78-79°C.has been used.

Raw material preparation:-

The straw collected was chopped to 1 inch length and leaves and sheath portion were separated by pneumatic separation technique. A proximate analysis of the rice straw was done according to Tappi Standard procedure. The results are given in Table 1.

Pulping process:-

Equipment: Round bottomed glass flask with water cooled condenser and electrical heating mantle was used for carrying out prehydrolysis and pulping.

The effects of pretreatment with water and dilute sulphuric acid were studied. It was found that, prehydrolysis with 1.5 % H_2SO_4 concentration around 100°C, for 1 hour at 1 atmospheric pressure was most effective. The prehydrolysed material was washed free from acid and taken for Organosolv pulping.

The pulping was carried out under 1 atmosphere pressure and the following parameters were studied to find the optimum conditions:

1. Cooking liquor - 1: 1 Ethanol - Water Mixture.
2. NaOH added on O.D. basis in percentage (0.5-12.0 %).
3. Cooking time 90 minutes to 240 minutes.

Table 2 gives the effect of NaOH and Table 3 gives the effect of time on Kappa No. and Yield. Also, Table 4 gives the mechanical strength properties of the obtained pulp at optimum conditions

To study the effect of lower bath ratio, moderately high temperature and pressure a pulping digester was designed and got fabricated for carrying out the further experiments. A sketch of the same is given in Fig. 1. The digester is made of stainless steel of 5 lit. volume and provided with water cooled condenser in the lid along with safety valve, pressure release valve, pressure gauge and thermometer. Pre-hydrolysis and pulping was carried out in this digester and the results are given in Table 5.

Observations: A discussion

Agricultural residues are by nature low in lignin content, and rice straw has 8-10 % lignin content which renders easy pulpability under milder conditions. The high silica content present in straws poses problems in conventional recovery, while it is not affecting the recovery process of solvent pulping.

As seen in Table 2 the alkali concentration has significant bearing on the residual lignin and pulp yield. Higher the alkali charge there is a considerable drop in Kappa No. as well as yield. For about 20 Kappa No. 6 % alkali charge is found to be desirable. The cooking time is another paramter controlling the delignification as seen in Table 3. A cooking time of 150-180 minutes is found to give acceptable yields and Kappa No.

From the results of pulping carried out in laboratory digester under pressure and higher temperature as shown in Table 5, it is evident that cleaner pulp is obtained with less than 0.5 % rejects and pulp is of uniform quality. Generally, the straw pulp along with fines, which have no papermaking value, affects the quality of the pulp adversely in viscosity and drainage properties. For this purpose, the pulp was screened to eliminate fines below 100 mesh and the resulting pulp showed a drainage time of 12 seconds which is fairly good level of drainage. The viscosity of pulp at 14.8 cP. is comparable to any standard pulp of agricultural residues and even hardwoods. It is interesting to note that an yield of 38.7 % of unbleached pulp after elimination of 100 mesh fines at 27.5 Kappa No. level is very favourable in comparison to conventional processed pulp yields.

After establishing the suitability of Organosolv pulping process for processing agricultural residues in respect of pulp yield and quality it becomes necessary to look into the aspect of chemical recovery and economical utilisation of by-products for making the process economically viable and technically feasible.

A preliminary study on recovery of solvent is being worked out and it is expected 90-95 % solvent recovery is possible by flash distillation and by the established technology. Much work is needed in this area and some of the leading laboratories are working on this. It is hoped that, a suitable

process will emerge. There is a good scope regarding utilisation of by-products as a source of extenders inpolymers and adhesives, as bio-fertilisers and pesticides, and such much of R & D work is needed in this field.

Conclusion

Organosolv pulping is an emerging process yet to make its mark by technical superiority and economic viability, much in the face of stiff competition from the estabilished processes. However, looking to the salient features offered by this process such as selective delignification, leaset degradation of carbohydrate, environmentally beneficial and above all, the process can fit into small scale to cope with the local availability of agricultural residues.

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TABLE 1

PROXIMATE ANALYSIS OF RICE STRAW*

ASH CONTENT, %	14.5
ALCOHOL-BENZENE SOLUBILITY, %	8.1
COLD WATER SOLUBILITY, %	13.7
HOT WATER SOLUBILITY, %	17.0
HOLOCELLULOSE (ASH CORRECTED), %	64.9
LIGNIN (ASH CORRECTED), %	9.0
1.0 % NaOH solubility, %	49.5

* BASED ON THE OVEN DRY MASS OF THE RAW MATERIAL.

TABLE 2

EFECT OF ALKALI ADDITION ON ORGANOSOLV PULP YIELD AND KAPPA NUMBER

Constant Conditions:-
Prehydrolysis: H2SO4 Con. = 1.5 %, Time, hr. = 1 Pressure atm. 1, Bath ratio = 1:30, Temp at B.P.

Pulping: Time, hrs. 3, Pressure atm. 1, Bath ratio = 1:15, Tem. at B.P.

NaOH ON STRAW %	SCREENED PULP YIELD, %	KAPPA NO.
2.5	48.5	40.5
4.5	47.6	26.0
6.5	45.0	18.5
8.0	38.3	21.6
10.0	36.6	21.4
12.0	35.7	19.9

TABLE 3

EFFECT OF COOKING TIME VARIATION ON ORGANOSOLV PULP YIELD AND KAPPA NO.

CONSTANT CONDITIONS:

Prehydrolysis: H_2SO_4 Conc. 1.5%, Bath Ratio 1:30, Time, HR. 1, Pressure atm. 1, Temp at B.P.

Cooking: NaOH, % - 6, Bath Ratio - 1:15. Temp. at B.P.Pressure

COOKING TIME IN MINUTES	SCREENED PULP YIELD, &	KAPPA NO.
90	50.2	40.3
120	47.6	30.6
150	46.7	18.5
210	45.9	18.6
240	42.5	16.4

TABLE 4

MECHANICAL STRENGTH PROPERTIES OF STANDARD HANDSHEETS*

PROPERTY	VALUE
FOLDING ENDURANCE, MIT	11
BREAKING LENGTH, MTRS.	4570
STRETCH, %	2.8
TEAR FACTOR	44.0
BURST FACTOR	24.2
VISCOSITY OF BLEACHED PULP cP (CED)	15.2
STRENGTH INDEX	1035

* BEATEN IN BALL MILL TO A FREENESS OF 67°SR.

TABLE 5

ORGANOSOLV PULPING CARRIED OUT IN LABORATORY DIGESTER

Prehydrolysis:	H_2SO_4 Conc. 1.5 %, Bath Ratio 1:30 Temp. 120°C, Time 60 Min.
Washed With hot water and Then with cold water.	
Pulping:	Mother Liquor 1:1 Ethanol NaOH Bath Ratio 1:7, Temp. 130 + 2°C., PRESSURE 4 kg/cm², NaOH ON CATALYST 0.2. %

PULPING RESULTS:

SCREENED PULP YEILD, %	38.7
KAPPA NUMBER	27.5
VISCOSITY (CED), cP	14.8
BRIGHTNESS OF UNBLEACHED PULP, %	32
INITIAL FREENESS °SR	25
DRAINAGE TIME, SECS. (BRITISH SHEETMAKING MACHINE)	12

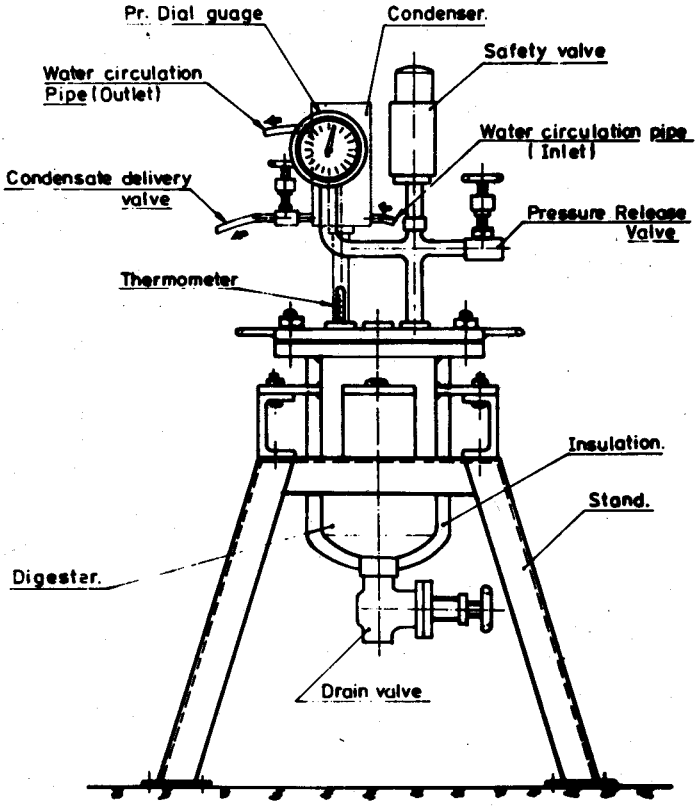

Fig 1. Laboratory Digester with Condenser for Organo Solve Pulping Process.