Acetic Acid Pulping and ECF Bleaching of Rice Straw and Effect of Acid Concentrtion on Pulp Characteristics

Sinha Akhouri Sanjay Kumar[1], Singh Manohar[1], Singh Surendra Pal[2]

1. Department of Chemical Technology, SLIET, Longowal, Sangrur, Punjab - 148106, INDIA.

2. Department of Paper Technology, Indian Institute of Technology, Roorkee, Saharanpur campus-247001, INDIA.

ABSTRACT

Acute shortage of conventional wood based & other fibrous raw materials for pulp and paper industry is one of the most challenging tasks in front of Indian pulp and paper industries to meet the growing demand of paper in India. Rice straw is available in abundant quantity in India and other Asian countries, so an environment friendly process apart from conventional soda and other pulping methods is required to convert rice straw from a biomass waste to a useful fibrous raw material for paper and allied industries. ***The chemical and mechanical processes have been explored to extract cellulosic fibers from rice straw.*** Rice straw is a fibrous lingo-cellulosic material which contains high amount of silicon dioxide (SiO_2). Rice straw burning in agricultural fields is a serious environment pollution problem in north India & other parts of world due to not finding proper utilization. Industrial utilization of rice straw will solve the problem of its handling and scarcity of fibrous raw material for pulp and paper industries. The catalyzed acetic acid pulping process conditions has been optimized using full factorial response surface methodology to separate fibers in environment friendly manner with low energy consumption. The D E D bleaching responses for the acetic acid pulp have been studied. The variation of ash and silica percentage with the increase of brightness of pulp has been observed.

Key Words: *rice straw, silica, acetic acid, opacity, brightness, burst strength, air pollution.*

Introduction

Proper utilization of the agro waste and industrial waste materials is the key of **s**ustainability of industrial and social growth. Scarcity of conventional wood based & other fibrous raw materials for pulp and paper industry is one of the most challenging tasks. Rice straw is available in abundant quantity in India and other Asian countries, so a suitable technology is required to convert rice straw from a biomass waste to a useful fibrous raw material. Nearly 36% of the paper production comes from the forest based raw material and the remaining from the non-conventional raw materials such as agro residues and waste paper [1]. Rice straw is a fibrous lingocellulosic material typical of most agricultural residues; it differs from most crop residues in its high content of silicon dioxide (SiO_2). Ash content on a dry weight basis ranges from 13 to 20%, varying according to the state of conservation of the straw after harvest. The potential environmental benefits of diverting rice straw from open-field burning is reduction of air pollutants such as VOC, SOx, NOx, and PM10, and also silica emissions, which are not specifically monitored but can be a health hazard [2]. Annual world rice (Oryzae sativa) production was about 618 million metric tons in year 2005. India and china produced 130 and 183 million metric tons respectively in 2005. More than 50 countries contribute to this sum with the production of at least 100,000 tons of rice annually [3]. For every ton of grain harvested, about 1.35 ton of rice straw remains in the field. About 5.6-6.7 ton per hectare (2.5-3 tons per acre) of dry straw is an average net production. Rice straw was usually disposed of by open-field burning because it is a cheap disposal method [4]. Fractionation analysis and the profile and mapping of silica by scanning electron microscope combined with an energy dispersive X-ray analysis (SEM-EDXA) indicated that the silica in the bleached pulp was located mainly in epidermal cells and not in other elements, such as fibers and parenchyma, and that the silica-rich epidermal cells were scattered throughout the pulp as single cells or in bundles [5]. The use of organic solvents for fractionation of woody materials has been greatly expanded during the past few years. The huge amounts of residual plant biomass considered as “waste” can potentially be converted into various different value added products like natural fibers used for paper making, bio-fuels and chemicals [6]. A variety of variations on acetic acid pulping have been developed over the years and several new acetic acid based processes are currently under development. The molecular weight characteristics of lignin from acetic acid based pulping of wood are described in relation to liquor composition and degree of delignification. It appears that rapid delignification is associated with removal of large lignin fragments [7]. Solvent pulping methods can be divided into "uncatalyzed", acid-catalyzed and base-catalyzed processes. The rates of acid-catalyzed processes appear to be governed by the hydrolysis of a-ether bonds in lignin [8]. Wood processing in HCl-catalyzed acetic acid media (Acetosolv pulping) provides an efficient way to separate the main fractions of the raw material. In a single step, delignification and hemicellulose degradation are reached with good selectivity. The economic feasibility of this approach depends on the recovery of two marketable pulping byproducts: lignin and furfural [9]. Furfural has a wide range of industrial applications and comparatively high Price. So it can significantly affect the feasibility of integrated strategies for utilization of lignocellulosic materials [10]. Hydrolysis of rice straw by dilute sulfuric acid at high temperature and pressure was investigated in one and two stages. Formation of furfural was function of the hydrolysis pressure, acid concentration, and retention time [11]. A study of rice straw for its suitability in paper industry using acetic acid has been done. But this study does not consider the interaction effects of factors which may be significant. It was found that higher concentration of acetic acid favours the removal of lignin and better quality of pulp [12]. The presence of silica in pulp helps in getting high opacity in specialty grades of papers like colour laminate base etc. which has been reported in TAPPI and IPPTA journals[13, 14].

Materials & methods: Rice straw was collected from the near-by farming fields of Sangrur, Punjab. The straw was washed, cleaned and dried. It was cut into small size of 10 mm. Delignification (pulping) reaction of rice Straw was carried out in small stainless steel air tight jars placed in lab digester at controlled temperature. Acetic acid was used as main chemical and H_2SO_4 was used as catalyst. Each experiment was carried out by taking 100 gm of oven dry rice straw cut into small pieces. After completion of reaction for a given time for that batch, the mass was cooled and then filtered out. The crude pulp was obtained above the screen medium and subjected to further processing for analysis. The experimental design was done by using RSM (response surface methodology) full factorial in design expert 8.0.1 software. The experiment factors taken into consideration are acetic acid concentration in pulping liquor, catalyst concentration, LSR (liquid to straw weight ratio), time and temperature. The responses studied are pulp yield, kappa number, holocellulose and klason lignin. The reactions were carried out in laboratory research digester having the indirect heating and temperature control device. The details are given in table1. The unbleached pulp was bleached by DED bleaching sequence.

Table1: Design of experiment (Full factorial) using Response surface methodology

Std.	Run	Factor A: Acetic acid (%)	Factor B: Catalyst (%)	Factor C: LSR	Factor D: Temperature (°C)	Factor E: Time (min.)	Response 1: Pulp Yield (%)	Response 2: Kappa No.	Response 3: Hollocellulose (%)	Response 4: Klason Lignin (%)
14	1	90	0.5	14	120	120	50.75	40.5	71.5	8.1
16	2	90	2	14	120	120	65	63	62	12.1
47	3	70	1.25	11	82.5	210	54.5	21.54	77.5	4.3
48	4	70	1.25	11	82.5	210	54.5	21.53	77.6	4.2
3	5	50	2	8	45	120	66	68	69.1	12.8
35	6	70	0	11	82.5	210	65	69	68.7	11.6
21	7	50	0.5	14	45	300	61.5	65	68	10.6
26	8	90	0.5	8	120	300	52	32.2	73	4.8
27	9	50	2	8	120	300	58	56	66	7.2
4	10	90	2	8	45	120	64	78	62	11.4
41	11	70	1.25	11	82.5	60	67.2	85	52	11.9
45	12	70	1.25	11	82.5	210	54.5	21.53	77.7	3.7
30	13	90	0.5	14	120	300	48	32	74	4.8
28	14	90	2	8	120	300	56	54	72	7.5

32	15	90	2	14	120	300	62	56	70	9
50	16	70	1.25	11	82.5	210	54.7	21.54	77.5	3.8
38	17	70	1.25	18.13	82.5	210	55	21	76.5	3.9
31	18	50	2	14	120	300	57	54.8	67	7.1
46	19	70	1.25	11	82.5	210	54.6	21.6	77.5	3.9
9	20	50	0.5	8	120	120	62	62	64	9.2
12	21	90	2	8	120	120	45	35	72	5.1
33	22	50	1.25	11	82.5	210	69	90	68	12.9
10	23	90	0.5	8	120	120	50.8	40	72.5	7.8
23	24	50	2	14	45	300	62.5	67	67.5	10.7
25	25	50	0.5	8	120	300	54.5	51	68.5	6.5
2	26	90	0.5	8	45	120	62	75	60	9.2
43	27	70	1.25	11	82.5	210	54.7	21.54	77.5	3.8
29	28	50	0.5	14	120	300	54.2	53.8	68.5	6.8
19	29	50	2	8	45	300	62.2	66.5	67.9	10.1
34	30	100	1.25	11	82.5	210	62	18.7	68	3.5
15	31	50	2	14	120	120	62.3	66	67	10.5
1	32	50	0.5	8	45	120	69	88	62	12.1
6	33	90	0.5	14	45	120	61	73	62	9
22	34	90	0.5	14	45	300	57.5	19.7	68	3.5
11	35	50	2	8	120	120	36	40	66.2	7.8
13	36	50	0.5	14	120	120	61	60	65	9
8	37	90	2	14	45	120	61	73	62	9
37	38	70	1.25	3.86	82.5	210	65	95	68	11.5
39	39	70	1.25	11	37.8	210	64.5	80	72	11.2

49	40	70	1.25	11	82.5	210	54.7	21.54	77.5	3.8
20	41	90	2	8	45	300	62	75	64	9.5
18	42	90	0.5	8	45	300	60.8	19.9	68.6	3.6
42	43	70	1.25	11	82.5	424.0	55.7	23.8	75.5	4.2
5	44	50	0.5	14	45	120	68.5	87	63.1	12
17	45	50	0.5	8	45	300	61.8	64	69	10.4
36	46	70	3.03	11	82.5	210	68	62	62	12.5
44	47	70	1.25	11	82.5	210	54.7	21.54	77.5	3.8
40	48	70	1.25	11	130.71	210	28	21.8	70	3.8
7	49	50	2	14	45	120	69	91	61	12.8
24	50	90	2	14	45	300	62	75	64	9.5

Pulp fibers produced by the reactions were classified in Bauer-Mcnett type fiber classifier for calculation of fiber length. An agitated pulp suspension is fractionated by means of a screening process employing vertical screens with increasing wire sieve cloth numbers. The screens are mounted in tanks arranged in cascade. The mass of the fibres retained by each screen and of those passing all the screens is determined and expressed as a percentage of the oven dry mass of the original sample. Brightness and opacity were measured using Tappi test method for the pulp obtained after converting in hand sheet form (Using lab sheet former) and air drying to 90% dryness.

Results & discussion:

Proximate analysis of rice straw is shown in Table 2. It shows that ash and silica percent in rice straw are 17.68 % and 13.33 % respectively, which are significantly higher in comparison to other fibrous raw material. This is a major problem in evaporation and combustion of black liquor obtained by conventional chemical pulping process using soda pulping or kraft pulping. Catalyzed acetic delignification can prove to be a alternative process for use of rice straw in paper industry as cellulosic fiber source due to quite lower dissolving of silica in spent liquor. The bulk density is 113.8 Kg/m^3, which is quite lower in comparison to wood chips.

Table 2: Analysis of rice straw (raw material)

S.NO.	Analysis	Avg. Value (with variation) for different samples
1.	1% NaOH Solubility	35.75 ± 2.81
2.	Ash in rice straw	17.48 ± 1.30
3.	Silica in rice straw	13.33 ± 1.06
4.	Alcohol benzene solubility of the raw material	10.75 ± 1.42
5.	Klason lignin in rice straw	17.34 ± 0.69
6.	Holocellulose in rice straw	55.35 ± 0.68
7.	Hot water solubility	13.49 ± 0.43
8.	Cold water solubility	7.25 ± 0.45
9.	Moisture content in rice straw	13.51 ± 0.98
10.	Bulk density of rice straw (Kg/m^3)	113.8 ± 2.8

The experimental results and optimization for the different responses have been shown below in different contour graphs. The variation of klason lignin with the variation of catalyst percentage and acetic acid concentration

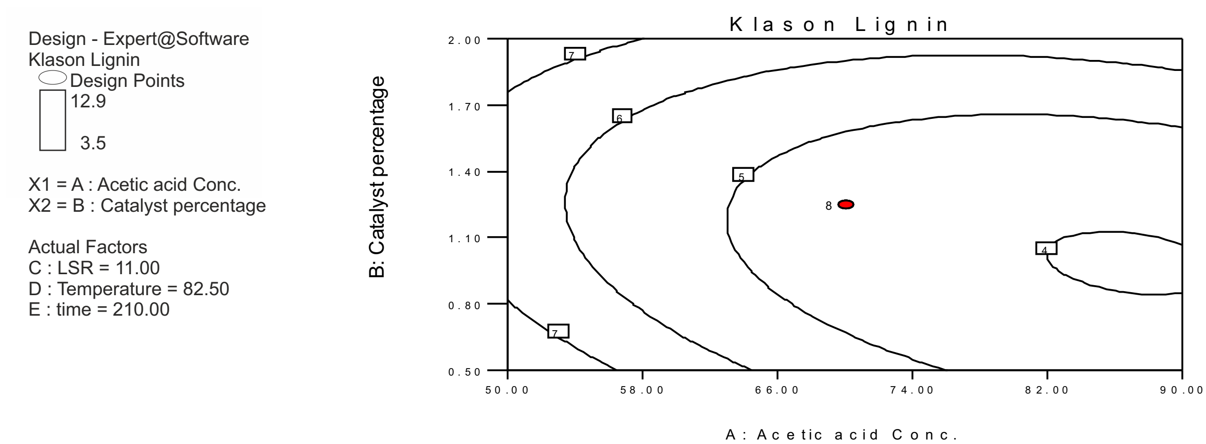

Figure1: Effects of acetic acid concentration and catalyst concentration on klason lignin (in pulp).

has been shown in figure 1. The value of other variables are shown on the side of the graph.

The variation of pulp kappa number, which tells about the degree of pulping and quality of pulp, has been shown in figure 2. The effects of the variation of catalyst percentage and acetic acid concentration are given at selected values of othe actual factors.

The variation of pulp Holocellulose, which tells about the quantity of cellulose and hemi-cellulose of pulp, has been shown in figure 3. The effects of the variation of catalyst percentage and acetic acid concentration on holocellulose are given at selected values of othe actual factors (time, temp. and LSR).

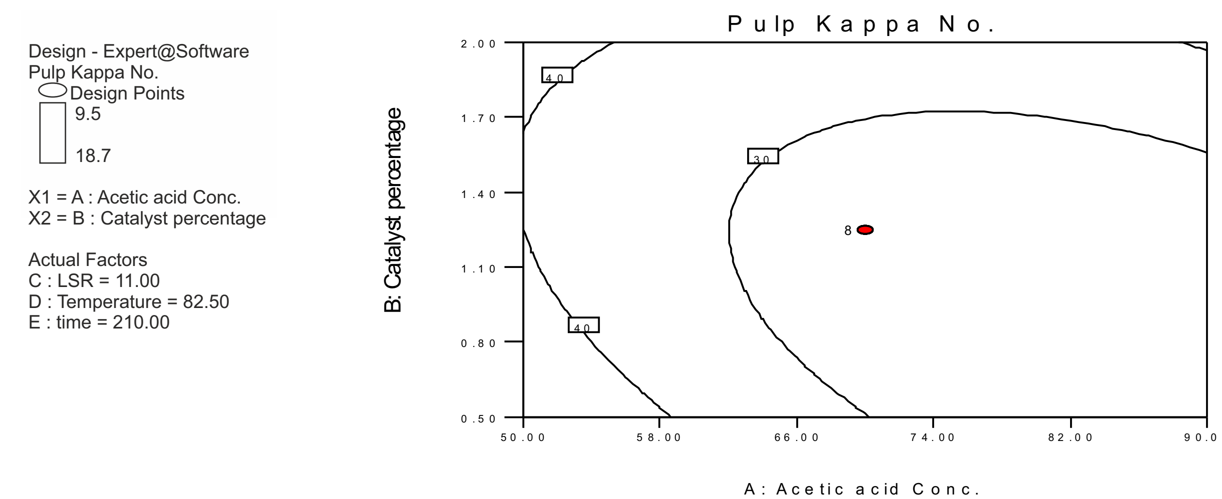

Figure2: Effects of acetic acid concentration and catalyst concentration on Kappa number (in pulp).

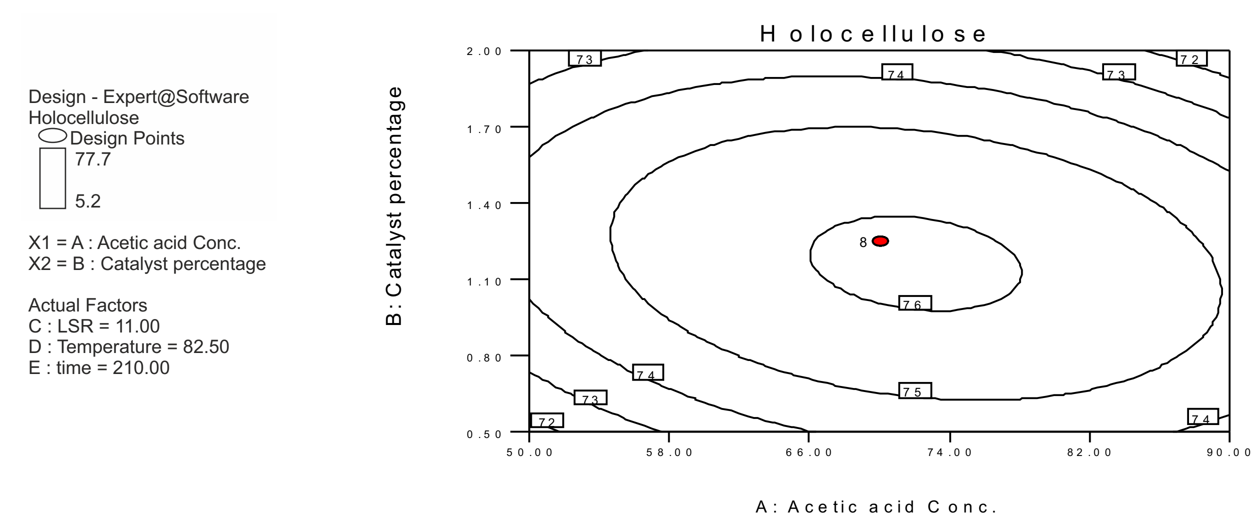

Figure3: Effects of acetic acid concentration and catalyst concentration on Holocellulose (in pulp).

The variation of pulp yield, which tells about the quantity of pulp produced as percentage of weght of rice straw used in the pulping process , has been shown in figure 4. The effects of the variation of catalyst percentage and acetic acid concentration on pulp yield are given at selected values of othe actual factors (time, temp. and LSR).

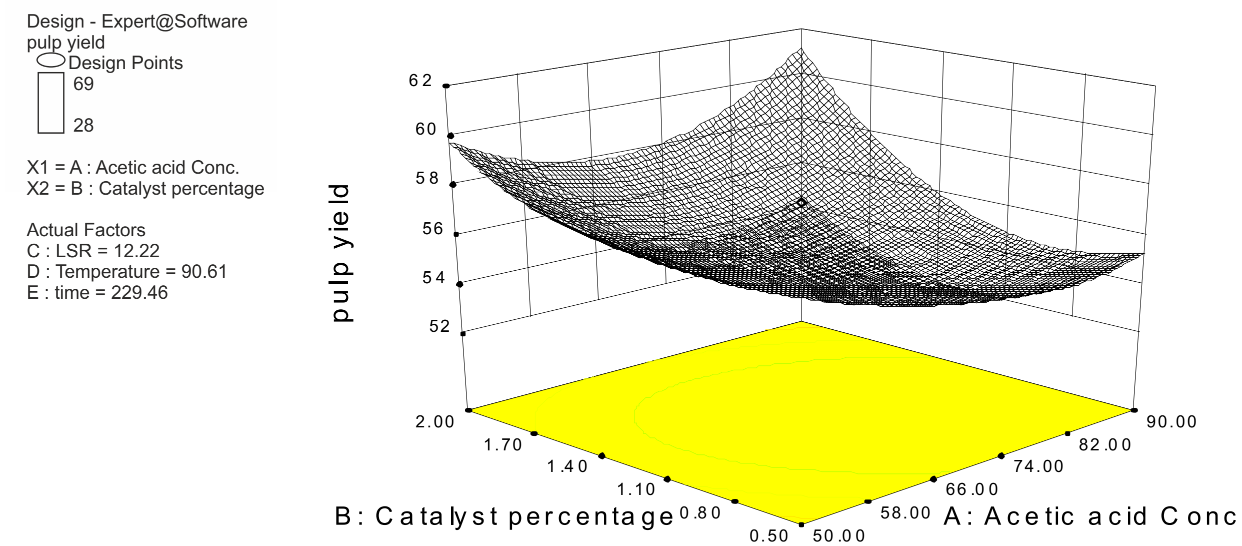

Figure4: Effects of acetic acid concentration and catalyst concentration on pulp yield

Economics of Optimized Pulping Conditions:

The optimum pulping condition was found as 76.72% of acetic acid concentration and 0.67% of H_2SO_4 concentration in the cooking liquor. The best bath ratio is 10.39. The optimum temperature of reaction is 78.81 °C and the required reaction time is four hrs and nineteen minutes. The higher amount of acetic acid increases the cost of pulping but this can be compensated by lower heat requirement in the process as temperature of reaction (78.81 °C) lower in comparison to temperature of soda or kraft process. The atmospheric pressure condition reduces the steam consumption. The recovery of chemicals is easy from spent liquor as lignin is easily precipitated by dilution with water, which brings down the cost of recovery process.

Analysis of Pulp:

Average weight fiber length of pulp, calculated by bauer Mcnett method is 0.82 mm. The detail fractionation is given in table 3. The brightness of unbleached paper (made of received pulp) is 26 - 27 % ISO (measured at 457 nano meters). The opacity of paper is 98%, which is very high and good for several grades.The burst index and tear index of sample paper is 0.6 -0.65 Kpa.m^2/g and 4.5 -4.7 mN.m^2/g respectively. The ash and silica present in the unbleached pulp are approximately 17 and 13 % respectively.

The spent liquor obtained after separation of the Pulp which can be easily filtered out using filter is the mixture of lignin, furfural, residual acetic acid and water. The lignin gets easily precipitated (due to insoluble character in water and large molecular size) on cooling of the spent liquor and separated from the rest. The acetic acid, furfural and water can be separated by distillation process. The acetic acid was separated by fractional distillation in lab and the strength was measured. The amount of recovered acetic acid was 202.5 gm/l. This can be reused in pulping process.

Table 3: Fractionation of pulp based on size of fibres

Sr. No.	Screen size(mm)	Oven dry Weight of pulp retained	Weight Fraction (%)
1	1.68	3.42	19.34
2	0.595	4.76	26.92
3	0.149	6.64	37.55
4	0.105	2.03	11.48
5	Fines < 0.105	0.83	4.69

Table 4: Stage wise increase of brightness of rice straw pulp (obtained by acetic acid pulping) and effect on ash and silica percentage in pulp

Bleaching stages	Chemical Dosing on the basis of O.D. pulp weight (%)	Kappa number of pulp obtained after bleaching	Brightness of pulp (% ISO)	Ash (%) on O.D. Pulp basis	Silica (%) on O.D. Pulp basis
Chlorine Dioxide bleaching (D_1 stage)	3	10.30	48.55	15.9	13.9
NaOH Extraction (E stage)	3.5	7.12	59.12	15.2	13.5
Chlorine Dioxide bleaching (D_2 stage)	2	6.20	82.31	14.8	13.3

The ash percentage and silica percentage decreases with increase of bleaching reactions but alkaline Condition has more severe impact on silica and ash percentage

Conclusion:

The experiments were targeted for getting the optimum range of kappa number of pulp (15-22), minimum residual lignin in pulp, maximum holocellulose and maximum yield of pulping process. As the higher holocellulose and optimum kappa number provides best quality of fibers for paper making. The higher yield provides most economical process of manufacturing. The optimum solution was found as 76.72% of acetic acid concentration and 0.67% of H_2SO_4concentration in the cooking liquor. A bath ratio, also called as liquid to solid ratio, was found to be best at 10.39. The optimum temperature and time are 78.81 ^oC and 259.13 minutes respectively. The optimum pulp yield obtained is 56.26 % with a pulp kappa number of 21. The pulp has a residual lignin percentage of 4% and an optimum holocellulose of 75.88%. The desirability of selected process conditions is 0.533. The pulp has the good mechanical strength and optical properties. So it is suitable for paper and paper board manufacturing. The DED bleaching sequence provides rice straw pulp with 82.3 % ISO brightness. The ash and silica percentages are 14.8 and 13.2 respectively. Approximately 90 % of ash is silica in the bleached pulp.

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