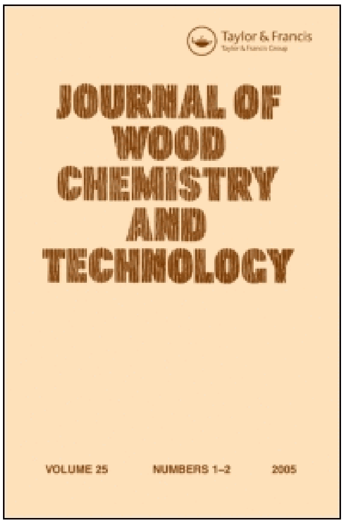

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THE USE OF LEWIS ACIDS DURING RAPID STEAM HYDROLYSIS

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ABSTRACT

Mixed hardwood chips were treated with various concentrations of aluminum chloride hexahydrate, aluminum sulfate hydrate, and ferric chloride and were subjected to rapid steam hydrolysis pretreatment (RASH). The three levels included 0.01, 0.03, and 0.05 moles of catalyst per 1000 grams of wood. Rapid steam hydrolysis (RASH) was done from 180° to 260°C at 20°C intervals for one minute. The Lewis acid catalyst affected the overall recovery yield of solids, the recovery values of the individual components, the enzymatic rates, and the methanol and water solubility. Overall recovery of pretreated solids generally decreased with the increase in levels of the catalyst. The one exception was $AlCl_3 \cdot 6H_2O$ where the minimum recovery levels were reached at 0.03 moles per 1000 grams of wood and increased at the higher level of catalyst. Cellulose degradation occurred in the temperature range of 250° to 260°C for the control and at the two lower concentrations of the catalyst. At the higher levels of catalyst, appreciable amounts of cellulose degradation occurred at lower temperatures. Hemicellulose solubilization and degradation were extremely sensitive to the RASH temperature and to the levels of catalyst. Almost all hemicellulose was lost at high temperatures or at high levels of catalyst. Losses of lignin appeared to be affected mainly by the RASH temperature and not by the changes in the levels of catalyst.

In contrast, both the temperature and the level of catalyst strongly affected the rates of enzymatic hydrolysis. Generally, the intermediate level of catalyst seemed to give the highest rates of enzymatic hydrolysis at the lowest temperature. Methanol and water solubles

increased in the presence of the catalyst and reached a maximum at levels of 0.03 moles between 230° to 250°C.

INTRODUCTION

In recent years, a variety of pretreatments have been evaluated for biomass conversion. The pretreatments have included steam explosion, organosolv, autohydrolysis, wet oxidation and rapid steam hydrolysis[1-9]. Processes that utilize steam or high temperature water treatment have several advantages compared to other physical or chemical processes[1,3,10,11,12]. These advantages include:

- The cost of chemicals (steam) is relatively cheap compared to any other chemical.
- The pretreatments can provide a fractionation of the wood components.
- The processes are effective in increasing the enzymatic rates of hydrolysis.
- Solid fraction obtained after these pretreatments contained a higher percentage of cellulose than the starting material.
- These processes appear to be effective with a wide variety of biomass materials.

The objectives of this study were to determine if the enzymatic rates could be increased, if the specificity of the reactions could be improved, and if the ability to separate the individual components could be enhanced by addition of Lewis acids.

More specifically, in this study three Lewis acids were evaluated as catalysts for RASH pretreatment. The acids included aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$), aluminum sulfate hydrate [($Al_2(SO_4)_3 \cdot 18H_2O$)] and ferric chloride ($FeCl_3$). Three different amounts of each catalyst were evaluated at RASH pretreatment temperatures of 180° to 260°C at 20°C intervals for one minute. The biomass materials used in this study consisted of mixed hardwood materials which are abundant in the southern United States[13,14]. The composition of the mixed hardwoods used in this study was 40.0% cellulose, 17.4% hemicellulose (based on monosaccharide analysis after hydrolysis), and 31.3% lignin (obtained with the Klason lignin procedure). The remaining material presumably consisted of acedic carbohydrates found in the xylan and extractives. No attempt was made to monitor the changes in concentration of these constituents during RASH pretreatment.

MATERIALS AND METHODS

Mixed hardwood chips of 1" - 1.5" were obtained from a commercial woodyard. A large amount of chips was ground and screened through a 6mm sieve. The chips were sprayed with three levels of catalyst (0.01, 0.03, and 0.05 moles/1000 grams of wood). The solution used to spray the chips was prepared by weighing the appropriate weight of catalyst in 100 ml of water. To insure a uniform distribution of the catalyst, the wood chips were continuously mixed for 2 hours while being sprayed with the solution.

After spraying, the wood chips were air dried for 24 hours prior to RASH pretreatment. The RASH pretreatments were done in the temperature range of 180° to 260°C at 20°C intervals for one minute. More detailed information on the RASH pretreatment can be found in a previous publication[14]. Following pretreatment, the solid fraction was air dried for 24 hours. After air drying, the pretreated material was weighed to determine percent solids and was stored in a refrigerator for further analysis.

The pretreated material was analyzed to determine the percentage of carbohydrates, Klason lignin, water and methanol soluble materials and to determine 72 hour enzymatic hydrolysis rates. The enzyme was a commercial product, Cellulase by Meiji Seika Co., Ltd., Japan. The enzymatic and analytical procedures are described in more detail in previous publications[1,3,14]. All values were based on the oven dryed weight of the starting material.

RESULTS AND DISCUSSION

The RASH process was used to evaluate three catalysts - $AlCl_3 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3$ - at various concentrations and temperatures. The relationships between the recovered solids and the reactor conditions are given in Table 1.

The amount of recovered solids decreased as the temperature increased for both the control (uncatalyzed) materials and the catalyzed materials. Compared to the control, the wood containing Lewis acids had lower solids after RASH pretreatment. Increasing the catalyst concentration resulted in lower solids in every case except the 0.05 moles $AlCl_3 \cdot 6H_2O$ treated material. A possible explanation for the increased level of solids is given in a later part of this paper.

The effects of the Lewis acids and the RASH temperatures on the individual chemical constituents are given in Table 2. Changes in the cellulose content, based on glucose analysis, are summarized in Figure 1 and in Table 2. Since all of these values are based on starting material, a direct comparison can be made between the values at various temperatures. The glucose units in the cellulose of the uncatalyzed material were stable up to 240°C. This result agrees with earlier results[1,3]. The material treated with 0.01 and 0.03 moles of the various catalysts behaved in the same fashion as the control and was stable up to 240°C. In contrast, all three catalysts at the 0.05 mole levels behaved differently. Compared to

TABLE 1
Percentage Solids After Rash Pretreatment Calculated Based on Starting Wood Weight

		$AlCl_3 \cdot 6H_2O$			$Al_2(SO_4)_3 \cdot 18H_2O$			$FeCl_3$		
TEMP°,C	CONTROL	.01m[a]	.03m	.05m	.01m	.03m	.05m	.01m	.03m	.05m
180	100.0	99.7	98.8	96.4	98.8	98.8	96.7	98.0	97.6	96.4
200	96.3	94.8	92.6	92.3	95.4	91.8	86.2	94.5	93.0	88.2
220	87.8	84.1	81.1	83.0	85.1	80.7	74.9	83.9	81.0	76.6
240	75.7	73.5	67.4	70.3	73.1	70.1	60.4	70.8	69.2	66.9
260	64.6	61.1	55.0	59.7	60.8	56.8	37.0	60.4	56.2	51.7

[a] m = moles of catalyst per 1000 g dry wood weight.

TABLE 2
Percentage Composition of RASH Pretreated Material Calculated Based on Starting Wood Weight

		$AlCl_3 \cdot 6H_2O$			$Al_2(SO_4)_3 \cdot 18H_2O$			$FeCl_3$		
TEMP°,C	CONTROL	.01m[a]	.03m	.05m	.01m	.03m	.05m	.01m	.03m	.05m
Cellulose[b]										
180	41.6	42.7	45.3	33.7	39.5	45.0	40.5	42.2	40.9	42.4
200	42.3	42.0	42.9	37.2	40.8	43.8	35.5	38.3	40.1	41.0
220	42.1	41.1	41.1	34.3	38.2	45.7	38.3	40.0	40.6	43.2
240	44.4	43.9	40.7	39.1	40.4	39.1	32.5	39.0	37.6	41.9
260	40.6	41.2	35.8	34.8	39.6	38.8	16.2	37.9	34.1	33.4
Hemicellulose[c]										
180	13.6	15.3	15.0	5.7	13.7	13.3	7.3	13.7	13.0	9.2
200	13.3	13.9	12.4	7.1	12.7	11.2	4.2	13.0	11.7	6.3
220	10.0	10.2	7.8	4.3	8.1	7.9	2.1	9.9	7.7	4.4
240	6.6	3.3	3.6	2.8	5.6	3.4	1.9	6.1	3.9	1.5
260	2.9	1.4	0.0	2.5	0.7	0.0	1.5	1.5	2.4	1.2
Lignin[d]										
180	32.1	31.0	31.3	39.1	33.2	32.8	37.3	31.5	27.1	35.7
200	28.7	32.0	31.1	33.5	31.9	30.8	33.9	31.7	28.7	33.4
220	28.7	29.4	30.1	29.9	31.3	29.1	29.3	29.4	26.5	29.1
240	24.5	25.1	27.6	24.4	26.7	26.4	24.4	23.0	23.7	25.6
260	20.5	20.8	21.7	19.4	20.2	21.2	17.2	20.2	18.4	17.8

[a] m = moles of catalyst per 1000 g dry wood weight.
[b] Based on glucose analysis after hydrolysis.
[c] Based on carbohydrate analysis after hydrolysis.
[d] Based on Klason-lignin values.

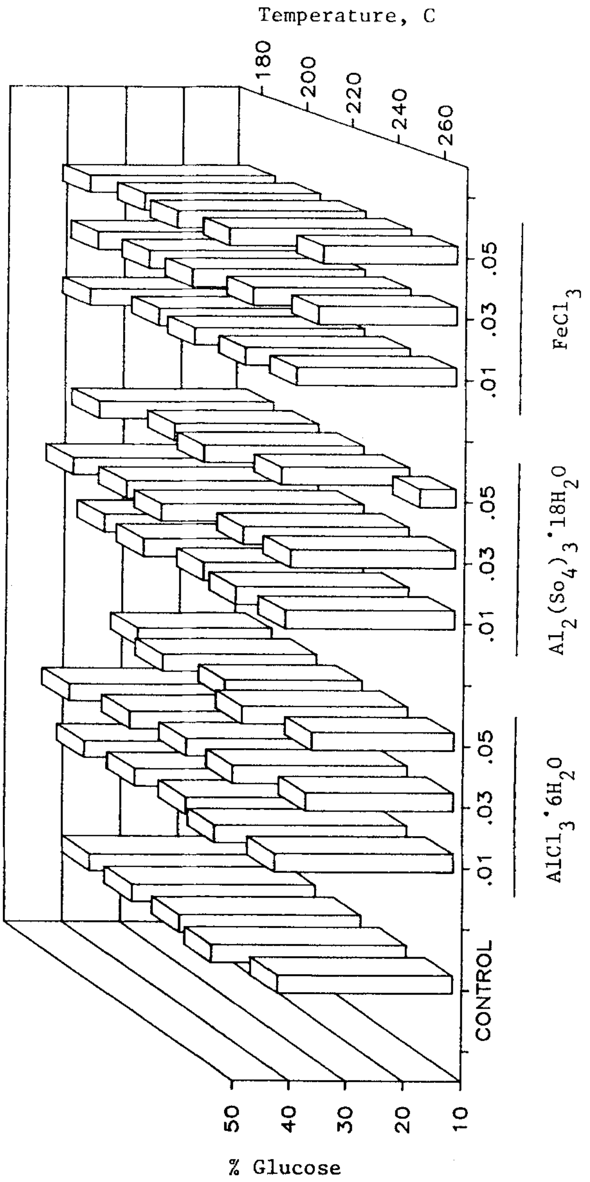

Figure 1. Glucose content after RASH pretreatment and hydrolysis calculated based on starting wood weight.

the control, the $AlCl_3 \cdot 6H_2O$ and the $FeCl_3$ treated materials had a lower cellulose content at all temperatures. The $Al_2(SO_4)_3 \cdot 18H_2O$ treated material lost more cellulose at 240° to 260°C than the other catalyzed systems. The cellulose in the $FeCl_3$ treated material was the most stable of the three treated materials; appreciable loss of glucose units occurred only at 260°C.

The changes in the hemicellulose components after pretreatment are given in Table 2. The original starting material contained approximately 17.5% hemicellulose, based on the total content of arabinose, xylose and mannose units. The control material pretreated at 180°C lost approximately 20% hemicellulose. In the control material, losses of the hemicellulose units increased with the temperature with the major losses of hemicellulose occurring between 220° to 260°C. In all three Lewis acids, addition of the catalyst resulted in increased losses of hemicellulose above 180°C. The losses generally increased as the concentration of Lewis acids increased. Overall, $Al_2(SO_4)_3 \cdot 18H_2O$ gave the largest hemicellulose loss at temperatures above 180°C.

The Klason lignin content of the various pretreated samples is reported in Table 2. For the control material, the lignin content decreased gradually as the RASH temperature increased. Approximately 35-38% of the lignin was lost at 260°C. Surprisingly, the Klason lignin content of the catalyzed systems was slightly larger than the control at low temperatures and was very similar to the control at high temperatures. This increase noted at low temperatures is probably due to hemicellulose and/or extractive degradation products which act like Klason lignin. Similar results have been found by other investigators[15,16].

The data in Table 1 shows that the total recovered solids generally decreased as the catalyst level increased. The one exception was the 0.05 moles $AlCl_3 \cdot 6H_2O$ treated material which had increased yields at temperatures of 220°C and above. In contrast, Table 2 shows the yields based on analysis of the individual components (Table 2), and the 0.05 moles $AlCl_3 \cdot 6H_2O$ yields decrease at all temperatures. There are several possible explanations for this apparent discrepancy. One explanation could be analytical error, but a more likely possibility is that low molecular degraded products from lignin or hemicellulose form insoluble complexes with the $AlCl_3 \cdot 6H_2O$. At the higher levels of catalyst, increased amounts of insoluble materials are formed.

Another important emphasis of this study was enzymatic rate values, which are valuable because they provide one method for hydrolyzing biomass and because they are a very sensitive indicator of physical and chemical changes of the lignin and cellulose during pretreatment. The results for 72-hour enzymatic hydrolysis are shown in tabular form in Table 3 and in graphic form in Figure 2. Values are based on the total available glucose in the material. The enzymatic hydrolysis rate for the control material increased gradually up to 220°C and then increased rapidly between 240°C and 260°C. The highest rate was observed at 260°C. An early study by Biermann[1] showed that a further increase of temperatures to above 260°C only slightly improved the rates. The material treated at the 0.01 mole level of catalyst had a slightly lower enzymatic rate than the control at all temperatures except 240°C. At the 0.03 mole levels up to 200°C, all three catalysts had approximately the same enzymatic rates as the control. Between 220°C and 240°C, the catalyzed material had a substantially higher enzymatic rate than the control. The optimum rates of enzymatic hydrolysis for the catalyzed material were obtained at 240°C; at higher temperatures,

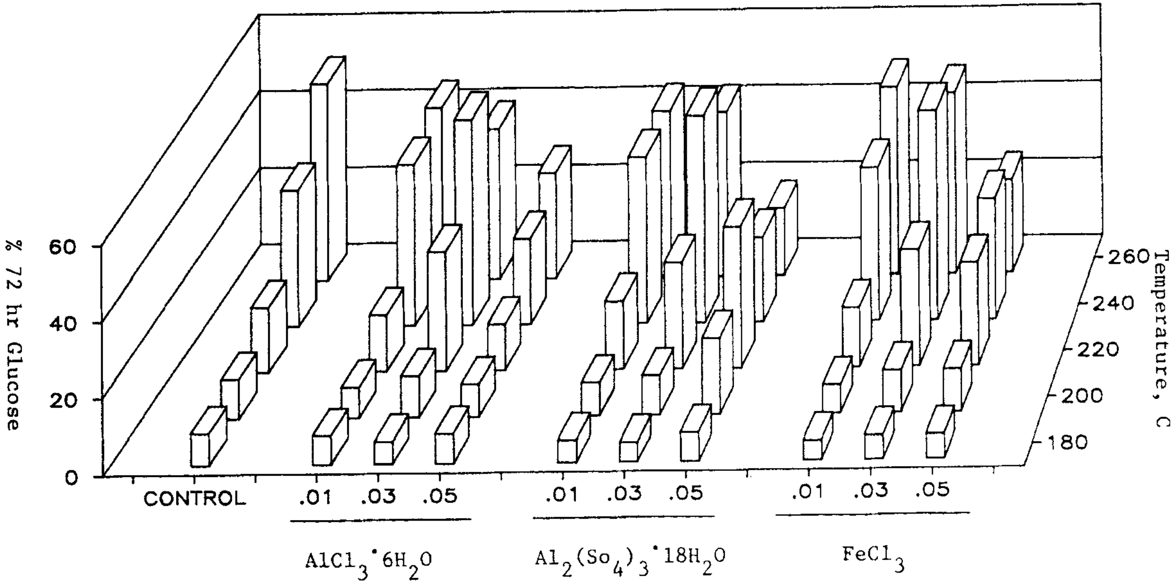

Figure 2. Rate of cellulose hydrolysis after treatment with RASH calculated based on starting wood weight.

TABLE 3
Percentage of Glucose After Enzymatic Hydrolysis (72 Hours)
Based on Starting Wood Weight

		$AlCl_3 \cdot 6H_2O$			$Al_2(SO_4)_3 \cdot 18H_2O$			$FeCl_3$		
TEMP°,C	CONTROL	.01m[a]	.03m	.05m	.01m	.03m	.05m	.01m	.03m	.05m
180	8.3	7.5	5.8	7.7	5.7	5.1	7.5	5.1	6.3	6.3
200	10.3	8.1	10.8	8.6	8.7	10.4	19.9	7.5	11.0	11.2
220	17.1	14.9	31.2	12.2	17.9	27.8	36.9	15.6	30.3	26.8
240	35.7	42.1	53.6	22.4	43.4	53.9	22.0	40.0	54.4	31.5
260	51.3	44.7	39.1	27.4	43.1	42.7	17.6	48.7	47.1	24.2

[a] m = moles of catalyst per 1000 g dry wood weight.

the rate decreased. At the highest level studied (0.05 mole), the enzymatic rates varied according to the type of catalyst. The $AlCl_3 \cdot 6H_2O$ catalyzed material had lower enzymatic rates at all temperatures compared to the control. The $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3$ treated materials had higher enzymatic rates at 200°C and 220°C but lower rates at all other temperatures. Apparently the optimum concentration of catalyst necessary to maximize the enzymatic rate is 0.03 moles. The results indicate that the maximum rates increased slightly in the presence of the catalyst, and the maximum rates occurred at approximately 20°C lower temperatures than the uncatalyzed runs. The enzymatic rates results also indicate that the amount of Klason lignin present had very little effect on the enzymatic rates.

The RASH pretreatment is not a very effective method for fractionating biomass components. For a commercial biomass conversion process, the RASH pretreatment would be followed with an extraction step to remove hemicellulose and lignin. In this study, two solvents - water and methanol - were evaluated to determine if the catalyzed RASH process increased the amount of soluble products. The results for methanol and water extraction are given in Table 4. The results indicate that the amount of methanol soluble materials is a function of the temperature, the type of catalyst, and the level of catalyst. At the lowest level of catalytic addition (0.01 moles), the percentage of methanol soluble material was similar to the control sample where the maximum level of soluble was obtained at 240°C to 260°C. At the intermediate catalyst level, the amount of soluble products increased at the lower temperatures of 180° - 220°C as compared to the control. At the highest level of catalyst addition, the percentage of methanol solubles varied depending on the catalyst. The $AlCl_3 \cdot 6H_2O$ material

TABLE 4
Percentage Solubles of RASH Pretreated Material[a]

		$AlCl_3 \cdot 6H_2O$			$Al_2(SO_4)_3 \cdot 18H_2O$			$FeCl_3$		
TEMP°,C	CONTROL	.01m[b]	.03m	.05m	.01m	.03m	.05m	.01m	.03m	.05m
MeOH										
180	1.3 (1.3)	1.9 (1.9)	2.5 (2.49)	2.3 (2.2)	1.0 (1.0)	2.0 (2.0)	23.4 (22.6)	1.7 (1.7)	3.5 (3.4)	4.7 (4.5)
200	3.0 (2.9)	2.6 (2.3)	7.8 (7.2)	2.9 (2.7)	3.7 (3.5)	7.1 (6.5)	25.4 (21.9)	1.8 (1.7)	6.5 (6.0)	12.6 (11.1)
220	5.6 (4.7)	7.5 (6.3)	14.5 (11.7)	9.0 (7.5)	9.8 (8.3)	13.9 (11.2)	12.0 (9.0)	4.5 (3.8)	12.5 (10.1)	19.2 (14.7)
240	16.3 (12.3)	13.4 (9.8)	16.9 (11.4)	13.6 (9.6)	15.4 (11.2)	16.7 (11.7)	8.9 (5.4)	11.9 (8.4)	17.2 (11.9)	19.0 (12.7)
260	18.9 (12.2)	15.2 (9.3)	14.9 (8.2)	12.4 (7.4)	14.4 (8.8)	16.3 (9.3)	27.3 (10.1)	15.4 (9.3)	16.7 (9.4)	21.0 (10.9)
Water										
180	2.2 (2.2)	4.2 (4.2)	9.5 (9.4)	1.6 (1.5)	2.8 (2.8)	3.9 (3.9)	11.4 (11.0)	1.5 (1.5)	5.4 (5.3)	6.4 (6.2)
200	4.0 (3.9)	4.6 (4.4)	14.3 (13.2)	5.0 (4.6)	6.0 (5.7)	8.1 (7.4)	19.2 (16.5)	3.7 (3.5)	8.3 (7.7)	11.7 (10.3)
220	6.1 (5.4)	11.2 (9.4)	16.4 (13.3)	10.2 (8.5)	11.2 (9.6)	11.4 (9.2)	12.7 (9.5)	7.5 (6.3)	13.6 (11.0)	10.1 (7.7)
240	11.9 (9.0)	11.6 (8.5)	11.9 (8.0)	11.5 (8.1)	12.6 (9.2)	10.2 (7.2)	8.5 (5.1)	9.9 (7.0)	10.8 (7.5)	14.2 (9.5)
260	9.4 (6.1)	7.7 (4.7)	11.0 (6.1)	10.0 (6.0)	17.0 (10.3)	8.0 (4.5)	15.2 (5.6)	6.6 (4.0)	8.3 (4.7)	9.6 (5.0)

[a] The results are shown based on both product and starting material (in parenthesis).

[b] m = moles of catalyst per 1000 g dry wood weight.

decreased as compared to the 0.03 mole level of the same catalyst, while the $FeCl_3$ treated material gave increased levels of methanol soluble material at all temperatures. The $Al_2(SO_4)_3 \cdot 18H_2O$ treatment at the 0.05 mole level appeared to be the most effective treatment, with very high levels of extractives, especially at the lower temperatures.

In this study, no attempt was made to identify the products removed by methanol. Since polysaccharides are not particularly soluble in methanol, most of this material is probably from degraded carbohydrates and lignin. This conclusion agrees with the compositional analysis of the materials (Table 2) which indicates that most of the hemicellulose is removed or degraded in the initial RASH pretreatment. Table 2 data suggests that removal of over 70-80% of the material at the higher temperatures or higher catalytic levels corresponds to the Klason lignin fraction. More detailed studies are now in progress to identify the materials removed by solvent extraction after catalyzed RASH pretreatment.

The percentage of water solubles of pretreated material is given in Table 4. The trends are similar to those observed for methanol soluble yields; however, the yields are generally lower than those obtained by methanol extraction. This result is probably due to the lower solubility of lignin and lignin degradation products in water.

This study indicated that addition of Lewis acids can strongly modify the RASH pretreatment of mixed hardwoods. Lewis acids can increase the breakdown rates of hemicellulose at low temperatures and the cellulose at high temperatures, but the acids do not affect the yield of Klason lignin. Enzymatic rates are improved by addition of Lewis acids, especially at the lower temperatures. The yields of products soluble in methanol and water are also increased at the lower temperatures by addition of Lewis acids.

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