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Production of amorphous silica and activated carbon from rice husk char obtained from two stage gasification process

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In this study the rice husk has been subjected to two-stage gasification to obtain syngas, tar and char. The rice husk char is subjected to alkaline extraction to obtain amorphous silica and activated carbon. The products have been characterized by methods such as BET, FTIR and XRF. The silica obtained from acid leached rice husk has BET specific surface area of 311.68 m^2/g and purity of 88.85%. The BET specific surface area of activated char increase from 102.49 m^2/g to 567.03 m^2/g after the activation process. The silica extraction using carbon dioxide (CO_2) precipitation is found to be more profitable than acid precipitation.

Keywords: Two-stage gasification, Pyrolysis, Rice husk char, Acid leaching, Amorphous silica, Activated carbon

Rice is an important cereal crop all over the world. Approximately, 506.3 million tons of rice was produced in 2019 throughout the world of which more than 20% is the husk[1]. Rice husk is the main agricultural by-products resulting from a rice processing industry. For every ton of rice being cultivated or processed approximately, 0.2 ton of rice husk is brought out as by-products[2]. Being of no nutritional value, rice husk cannot be used in the nutritional field. Hence, the problem of waste management arises. The importance of the need becomes graver since huge pollution has been created due to the open combustion of the same. Many researchers have focused their efforts on the possible uses of rice husk and rice husk ash due to their cheap cost as industrial wastes[3,4]. Rice husk contains approximately 21% of rich husk ash (RHA) which contains around 95% of the silica[5]. The necessity of managing rice by-products in huge amount as well as the idea of extraction of more value added products from rice leads to research on silica extraction from rice husk. The most conventional pretreatment is leaching the rice husks with various chemical agents to remove impurities. Leaching rice husks with acids and alkalis, such as HCl, HNO_3, H_2SO_4, H_3PO_4, CH_3COOH, NaOH, KOH, $Ca(OH)_2$ and even $KMnO_4$, before thermal treatment results in high purity amorphous silica (Bakar *et al.*[6], Selvakumar *et al.*[7], Ghosh and Bhattacharjee[8], Rhaman *et al.*[9]). Bakar *et al.*[6] performed the combustion of un-leached and acid leached rice husks in a muffle furnace at different operating temperatures in the range 500 - 900°C. The leaching of rice husk with HCl and H_2SO_4 was carried out to obtain amorphous silica with purity more than 99%. The effects of HNO_3 and H_2SO_4 on the size of silica particles was carried out by Selvakumar et al.[7] The combustion of rice husk at 700°C followed by acid leaching was carried by Ghosh and Bhattacharjee[8] to remove minerals from rice husk char and activation of char using CO_2. They also studied the process parameters optimization for production of precipitated silica and activated carbon from rice husk. The pyrolysis of rice husk at 700°C was carried out by Rhaman *et al.*[9] to obtain rice husk char followed by KOH activation to obtain activated carbon and alkaline extraction to obtain silica. Kalapathy *et al.*[10] developed a method to produce pure silica xerogels with 93% silica from rice husk ash having minimal mineral contaminants. Alvarez *et al.*[11] studied the overall valorization of rice husk char obtained by flash pyrolysis in a conical spouted bed reactor (CSBR) in a two-step process. Acid leaching and the two-stage gasification methods of rice husk were investigated to obtain the syngas, rice husk char and silica[12-15]. The aim of this study is to investigate the effect of acid leaching on the purity of silica, surface area of silica and composition of syngas. The effect of the activation process on the surface of carbon residue is also analyzed and then cost comparison was done for precipitation of silica using CO_2 and HCl.

Experimental Section

Acid leaching for silica extraction

Silica was extracted from pyrolysis char by using the alkaline method. The sample was digested in NaOH solution and then neutralized by the addition of HCl, which resulted in the gelation of silica. The process as shown in Fig. 1 is discussed in detail in our earlier study[13]. The acid leaching was carried out before extraction of silica to improve the purity of silica with minimum mineral contaminants[7,11]. In first case the acid leaching was carried out on grinded rice husk sample while in the second case the acid leaching was carried out on the char obtained after the gasification process. The purity of silica extracted in these cases was compared. In the first case, the rice husk was treated with 0.5 N HCl for 30 min at 60°C. The residue was washed to remove any contaminants. The washed residue was then dried in a hot air oven at 110°C for 12 h. Then the gasification and the silica extraction process were performed. In the second case, the rice husk char obtained after gasification was added to 100 mL water and the *p*H of the solution was

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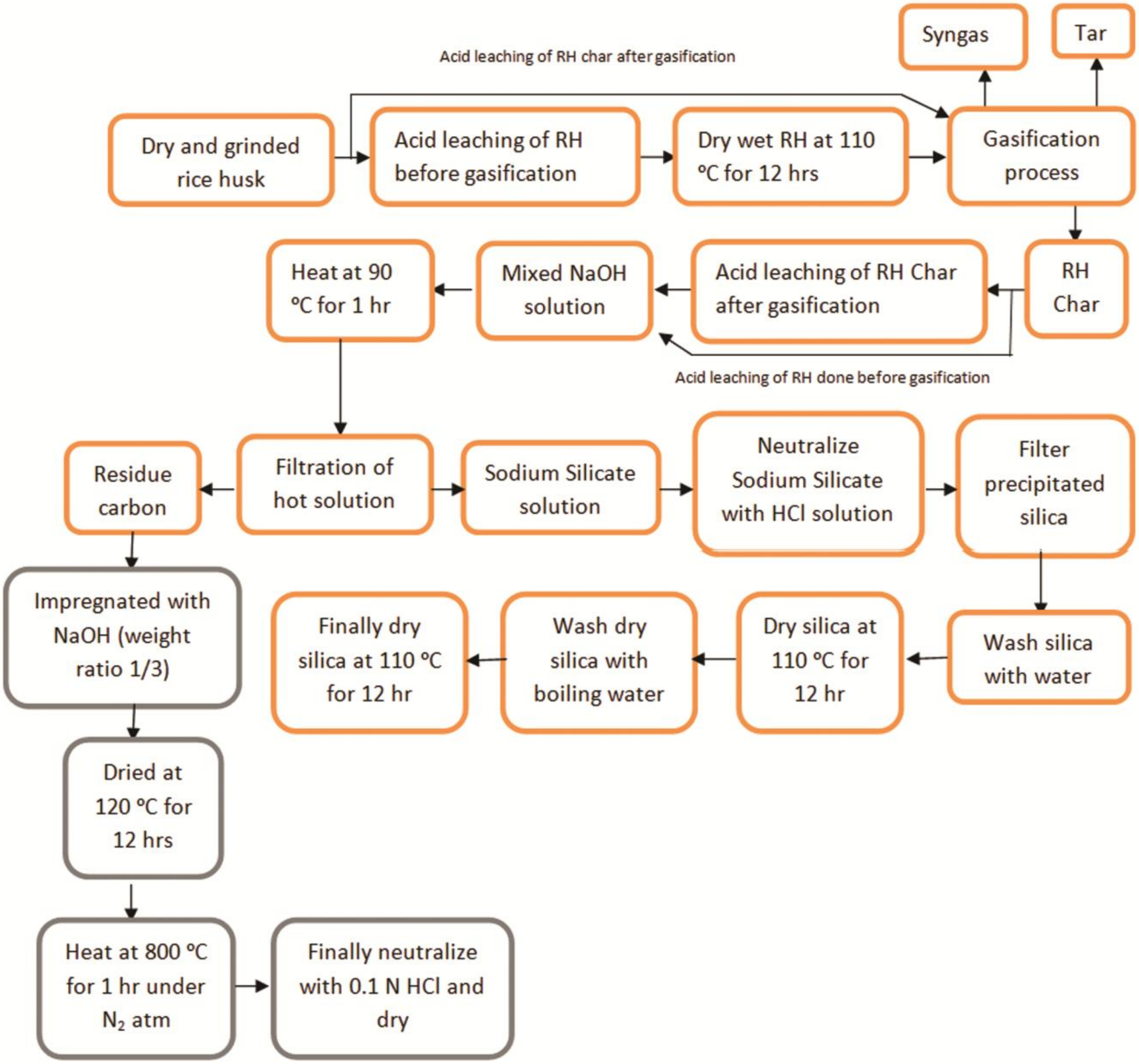

Fig. 1 — Process flow diagram for acid leaching, silica precipitation and carbon activation.

adjusted to 2. The suspension was then heated for 2 h at 75°C and filtered. The residue was washed to remove any contaminants. The silica extraction using hydrochloric acid solution was same as reported in our earlier study[13].

Preparation of activated carbon

The activation of carbon by NaOH has been studied by earlier researchers[16,17]. The process flow diagram for activation of carbon is given in Fig. 1. In this study carbon was impregnated with NaOH with weight ratio 1:3 (5 g carbon and 15 g NaOH). Then carbon dried at 120°C for 12 h. Then it was heated at a constant temperature of 800°C for 1 h under a nitrogen atmosphere at a flow rate of 0.5 L per hour in the first stage of the reactor. The obtained carbon was neutralized using 0.1 N HCl solutions and washed several times with water to *p*H ~7. Finally, it was dried at 110°C for 12 h. The surface area was analyzed using BET technique.

Precipitation of silica using CO_2

As shown in Fig. 2, silica extraction by CO_2 precipitation has the similar process as that of acid

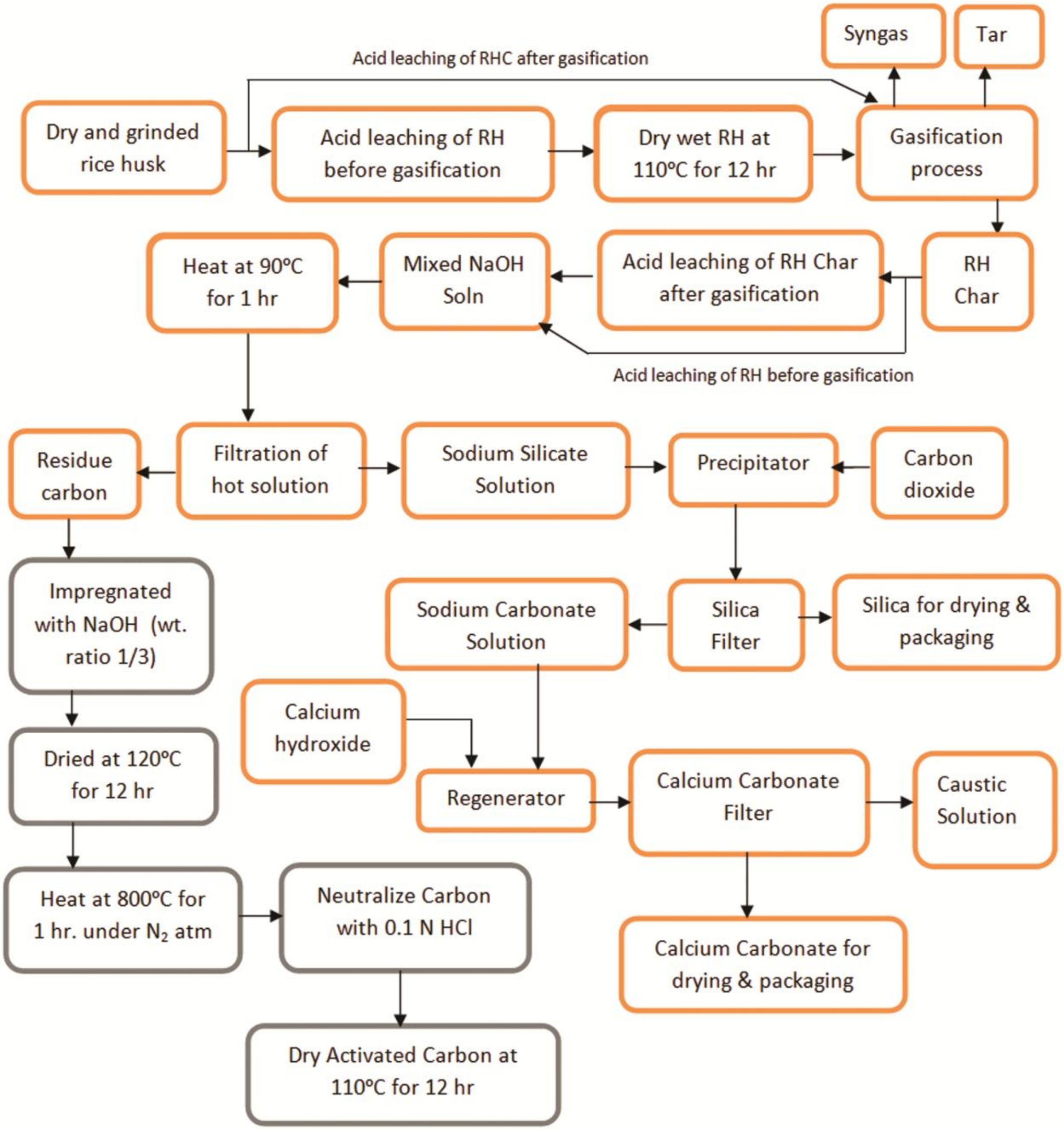

Fig. 2 — Process flow diagram for silica preparation by CO_2 precipitation method.

precipitation. The silica precipitation by CO_2 consists of three steps which include digestion, precipitation and regeneration.

Digestion: The carbon residue was dispersed in 1 N of 60 mL NaOH. The solution was stirred at 90°C for 1 h. The carbon residue and sodium silicate solution were obtained by filtration of this solution. Further treatment was given to carbon to obtain activated carbon.

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

Precipitation: To precipitate the silica, CO_2 gas was purged through the sodium silicate solution at a rate of 0.5 LPM. During this process CO_2 reacts with sodium silicate to form sodium carbonate and precipitated silica. Further precipitated silica and sodium carbonate solution were separated by filtration. The sodium carbonate solution was used for NaOH regeneration. Silica was washed with water two-three times and dried.

$Na_2SiO_3 + CO_2 \rightarrow Na_2CO_3 + SiO_2$

Regeneration: The sodium carbonate solution produced in the above step is used for the regeneration of sodium hydroxide by the following reaction.

$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$

As calcium carbonate is insoluble in water, it can separated by filtration. The remaining sodium hydroxide solution can be reused in silica extraction. So, regeneration helps in saving cost invested in sodium hydroxide as well as to save water. Also, calcium carbonate is a valuable product in the market.

Results and Discussion

Effect of acid leaching on purity of silica at different conditions

The purity of silica at different conditions were analysed using XRF. Acid leaching of rice husk and the rice husk char was carried out for removing metallic impurities. The experiments were carried out for XRF analysis of silica in different conditions of acid leaching as reported in Table 1. At first set of experiments, un-leached rice husk char obtained after gasification was used directly for silica extraction. In this case the purity of silica was found to be 83.86 %. At second set of experiments, the acid leaching of rice husk was done before gasification. In this case it was observed that the purity of silica increases to 88.85 %. At third set of experiments, the char obtained in the first stage of the reactor after gasification of rice husk was leached with acid before silica extraction. In this case the purity of silica was found to be 88.46 %. The XRF analysis shows that the acid leaching improves the purity of silica and found to be nearly same for second and third set of experiments irrespective of acid leaching before and after the gasification. In case of acid leaching, the purity of silica was more as compared to un-leached rice husk. This may be due to the removal of impurities such as Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O and Cl due to acid leaching of the samples[5].

Effect of acid leaching on surface area of silica at different conditions

As explained above the acid leaching of rice husk was done before and after gasification process. The acid leaching of rice husk before gasification gives more surface area of silica (311.68 m^2/g) as compared to acid leaching of the rice husk char after gasification (276.91 m^2/g). This is because in the acid leaching process before gasification, the hydrolysis of hemicelluloses and cellulose into smaller molecular weight compounds took place which could decompose during combustion and results in more surface area of silica particles.

Effect of acid leaching on composition of syngas

Figure 3 shows the effect of acid leaching on the composition of syngas. It is observed that the acid leaching of rice husk before gasification improves the composition of syngas. The acid leaching of rice husk (RH) before the gasification increases the volume percentage of hydrogen (H_2) from 23% to 24% and carbon monoxide (CO) from 27% to 30% as

Table 1 — XRF analysis of silica at different conditions, in weight %

Elements %	Un-leached silica	Acid leaching before gasification	Acid leaching after gasification
SiO_2	83.86	88.85	88.46
Na_2O	0.27	3.25	1.75
MgO	1.01	0.01	0.3
Al_2O_3	0.27	0.15	0.1
P_2O_5	-	0.008	0.09
SO_3	0.05	0.01	0.04
K_2O	0.03	0.03	0.13
SrO	0.006	-	-
Fe_2O_3	0.03	0.03	0.04
CuO	-	-	-
NiO	-	-	0.003
MnO_2	0.02	-	0.04
Cr_2O_3	-	-	0.007
CaO	2.21	0.03	0.59
TiO_2	0.01	0.005	0.01
Cl	0.14	0.71	0.27
LOI	11.76	6.57	7.86

compared to un-leached rice husk (RH). Also, the volume percentage of carbon dioxide decreases to 31% from 34.5% in the case of acid leaching of rice husk (RH) before the gasification. Hydrogen and carbon monoxide are combustible gases. Oxygen supports to combustion and carbon dioxide does not support to combustion and incombustible. The quality of the syngas ($CO+H_2$) improves by the acid leaching process because of hydrolysis of hemicelluloses and cellulose into smaller molecular weight compounds which could decompose easily during combustion. In both cases of gasification the methane formation was not observed. This may be due to the fact that as the reaction is carried out at 900 °C, the following steam reforming reaction is more pronounced leading to the formation of more hydrogen and carbon monoxide. The similar results were also observed in our earlier study[18].

$$CH_4 + H_2O + (\text{heat}) \longrightarrow CO + 3H_2$$

Effect of activation process on surface area of carbon residue

Carbon residue separated in the silica extraction process was activated using chemical activation process. The process of activation of carbon is described in Fig. 1. The surface area of activated carbon was measured using BET surface analysis. It is found that after activation the surface area of carbon increases five to six times to 567.03 m^2/g as compared to the surface area before activation of 102.49 m^2/g.

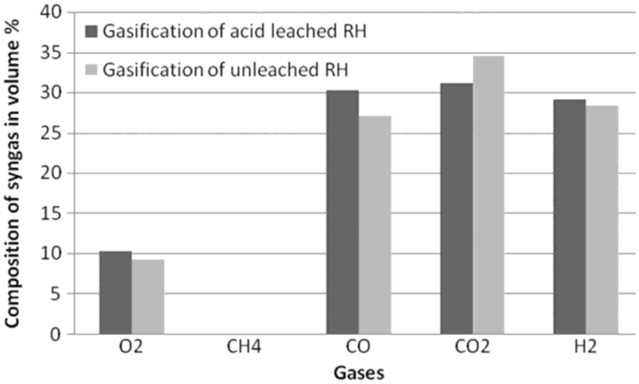

Fig. 3 — Effect of acid leaching on the composition of syngas.

Cost estimation

The cost estimates for reactor operation and silica extraction were calculated using electricity consumption and material balance in the silica extraction process respectively. The resistance of reactor heating coil was found out using an electronic multimeter and voltage across the coil was 220 volts. So, power consumption of the stage was found out using the formula $(\text{Voltage})^2/(\text{Resistance})$. Electricity consumption in a unit was found using multiplication of power in kW and time in hrs. Table 2 shows the reactor operation cost while Table 3 shows the cost of raw material and product. The cost required for silica preparation by acid and CO_2 precipitation methods was compared in Table 4. It is found that the silica extraction using CO_2 precipitation is more profitable than acid precipitation because of recovery of sodium hydroxide and formation of calcium carbonate a valuable product in this process.

Table 3 — Cost of raw material and product

Material Cost		
Material	Quantity	Cost (Rs)
NaOH	1 kg	30
HCl	1 kg	12
CO_2	1 kg	15
$Ca(OH)_2$	1 kg	12
$CaCO_3$	1 kg	35
NaCl	1 kg	10
SiO_2	1 kg	50
Activated Carbon	1 kg	40
Electricity	1 Unit	5.0549

Table 2 — Reactor operation cost

Operating Cost					
Stage	Voltage (Volt)	Resistance (Ohm)	Power (kWatt)	Time (hrs)	Unit
Stage-I	220	70	0.6914	0.25	0.1729
Throat Section	220	70	0.6914	0.6	0.4149
Stage-II	220	35	1.3829	0.6	0.8297
			2.7657	Total unit	1.4174
				Price/unit (Rs.)	5.0549
				Total cost (Rs.)	7.1650

Table 4 —— Comparison of cost of silica extraction by acid and CO_2 precipitation

Silica extraction by acid precipitation

Input Cost			Output Cost		
Material	Quantity	Cost (Rs)	Material	Quantity	Cost (Rs)
NaOH	12 g	0.36	NaCl	18 g	0.18
HCl	25 ml	0.36	SiO_2	9 g	0.45
Electricity	0.125 Unit	0.631	Activated Carbon	12 g	0.48
Total Cost (Rs)		1.351	Total Cost (Rs)		1.11

Silica extraction by CO_2 precipitation

Input Cost			Output Cost		
Material	Quantity	Cost (Rs)	Material	Quantity	Cost (Rs)
NaOH	12 g	0.36	SiO_2	9 g	0.45
CO_2	15 g	0.225	Activated Carbon	12 g	0.48
$Ca(OH)_2$	11 g	0.132	$CaCO_3$	15 g	0.525
Electricity	0.125 Unit	0.631	NaOH	12 g	0.36
Total Cost (Rs)		1.348	Total Cost (Rs)		1.815

Conclusions

The amorphous silica has been obtained by alkaline extraction of char obtained from two-stage gasification of rice husk. The BET specific surface area of acid leached sample is found to be 311.68 m^2/g. The XRF analysis results of silica samples obtained from acid leached and unleached rice husk samples gives a general idea that purity of silica samples obtained from acid leached rice husk is 88.85% which is purer than the ones from unleached rice husk with purity 83.86%. The acid leaching of rice husk results in more production of hydrogen and carbon monoxide as compared to the un-leached rice husk. Also, it is found that nitrogen is a better pyrolysing agent and that acid leaching is to be done on rice husk sample to obtain higher purity silica. The cost estimation study shows that the silica extraction using CO_2 precipitation is more profitable than acid precipitation.

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