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# Synthesis of *Jatropha curcas*-based Methyl Ester and Ethyl Ester as Biodiesel Feedstocks

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## ABSTRACT

Research on the use of *Jatropha curcas* triglycerides as biodiesel feedstock has received worldwide attention due to its inherent characteristics. Unlike palm oil, J. curcas oil is not edible, and thus, it will not disturb the food supply. However, to the researchers' experiences with the synthesis of J. curcas, oil-based biodiesel has shown that the fuel characteristics depend largely on the type of alcohol used as the excess reactants. Transesterification reaction is chosen for this process with sodium methoxide as the catalyst. Comparison studies on the yield of esters using methanol and ethanol, as well as the impacts on the reaction rate are discussed. The effects of reaction time and molar ratio on the reaction conversion are also examined. The determination of reaction yield is based on the conversion of triglycerides into alkyl esters as the main product. The findings are described as follows: the highest percentage yield of product is attained at 96% for methanol as an excess reactant, and this is 90% when ethanol is used. The optimum conditions of parameters are achieved at 6:1 molar ratio of alcohol to triglycerides, 50 min of reaction time and reaction temperature of 65°C for methanol and 75°C for ethanol. The biodiesel properties of both ester fuels were determined according to the existing standards for biodiesel and compared to the characteristics of diesel fuel.

**Keywords: *Jatropha curcas* triglycerides, methyl ester, ethyl ester, catalyst**

## INTRODUCTION

Biodiesel is the product of the transesterification reaction between vegetable triglycerides and alcohol. It possesses many advantages as it is derived from a renewable and domestic resource. Among liquid bio-fuels, biodiesel is gaining acceptance and market share as diesel fuel (Demirbas, 2003). As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel. Compared to fossil-based diesel, biodiesel has a more favourable combustion emission profile, such as low emission of carbon monoxide, particulate matter and unburned hydrocarbon (Zhang *et al*., 2003).

As one of the domestic commodities, vegetable oils have the potential to substitute a small fraction of petroleum distillates and petroleum based petrochemical in the future. According to Srivastava and Prasad (2000), the use of vegetable oil, such as palm, soy bean, sunflower, cotton seed, peanut, rapeseed, corn and castor oils as alternative fuels for diesel engines, dated back to almost nine decades ago. Generally, biodiesel feedstock was treated by using certain process technology to reduce the viscosity of product. The vegetable oil, triacylglycerol or is often called triglycerides, is a mixture of fatty acid triesters of glycerol (Tapanes *et al*., 2008). The most common method used

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to produce biodiesel is by transesterification which refers to a catalyzed chemical reaction involving vegetable triglycerides and alcohol to yield fatty acid alkyl esters and glycerol as by-product (Zhang *et al*., 2003). Another term for this particular process is alcoholysis. This reaction method is carried out under atmospheric condition and the stepwise of reaction is as shown in equations (1) to (3). Normally, transesterification can be catalyzed by both homogeneous and heterogeneous catalysts.

$$TG = ROH \xleftrightarrow{catalyst} DG + R'COOR \quad (1)$$

$$DG + ROH \xleftrightarrow{catalyst} MG + R'COOR \quad (2)$$

$$MG + ROH \xleftrightarrow{catalyst} GL + R'COOR \quad (3)$$

where TG, DG, MG, GL, R and R' denote triglycerides, diglyceride, monoglyceride, glycerol, alkyl and long hydrocarbon chain, respectively.

Alkali catalysts are the most common, since the process is faster and the reaction conditions are moderate (Freedman *et al*., 1984). Barnwal and Sharma (2005) reported that the alkali metal alkoxides are found to be effective transesterification catalysts as compared to acidic catalysts. Potassium and sodium hydroxide are the familiar homogeneous alkali catalysts applied in the transesterification of oil with very low free fatty acid content. The fatty acid composition of various types of vegetable triglycerides is given in Table 1. The characteristics of the triglycerides depend largely on the type of fatty acids present in the oil. Table 1 shows that *Jatropha curcas* and other vegetable triglycerides contain high percentages of unsaturated compounds, except for palm triglycerides. This finding indicates that these vegetable triglycerides are suitable to be used as biodiesel feedstock, specifically for low temperature applications. The catalyst type and loading required for the reaction are also dependent on the feedstock.

TABLE 1
The chemical composition of vegetable triglycerides (Sources: [b]Tapanes *et al*., 2008; [c]Crabbe *et al*., 2001; [a]Srivastava & Prasad, 2000)

| No | Vegetable triglycerides | Fatty acid composition, wt % | | | | |
|---|---|---|---|---|---|---|
| | | 16:0 | 18:0 | 18:1 | 18:2 | 18:3 |
| 1 | *Jatropha curcas*[b] | 16 | 6-7 | 42-43.5 | 33-34.4 | >0.80 |
| 2 | Palm[c] | 41-47 | 3.7-5.6 | 38.2-43.5 | 6.6-11.9 | 0.5 |
| 3 | Corn[a] | 12 | 2 | 25 | 61 | 0 |
| 4 | Cottonseed[a] | 28 | 1 | 13 | 58 | 0 |
| 5 | Peanut[a] | 11 | 2 | 48 | 32 | 1 |
| 6 | Rapeseed[a] | 3 | 1 | 64 | 22 | 8 |
| 7 | Sunflower[a] | 6 | 3 | 17 | 74 | 0 |
| 8 | Soy bean[a] | 12 | 3 | 23 | 55 | 6 |
| 9 | Mahua[a] | 16-28.2 | 20-25.1 | 41-51 | 8.9-13.7 | 0 |

Another important parameter in the selection of suitable vegetable oils for biodiesel feedstock is the FFA content of the feedstocks. In particular, feedstock with high content of FFA will trigger the incidence of saponification reaction to produce soap emulsion of which shall reduce the biodiesel yield and affect the recovery of the by-product (Schuchardt *et al*., 1997). To avoid saponification reaction, the FFA content of feedstock should be less than 1.0% (Tiwari *et al*., 2007). Berchmans and Hirata (2007) reported that the quality of *J. curcas* oil was degraded due to poor handling and long storage period prior to utilization. Various chemical reactions, such as hydrolysis, polymerization

and oxidation, cause deterioration in the quality of oil. The increase of free fatty acid value was due to the hydrolysis of triglycerides in the presence of moisture and oxidation. The triglycerides should be treated via acidic pre-treatment step to lower the percentage of FFA and improve the quality so that it could be used directly as the feedstock for biodiesel production (Azhari *et al*., 2008).

The main objective of this experimental work was to determine the optimum condition for biodiesel production using two types of alcohol derivatives, namely methanol and ethanol. Finally, the properties of the biodiesel were analyzed according to the standard methods.

## MATERIALS AND METHODS

### *Materials*

*Jatropha curcas* oil (triglycerides) was produced using a multi-purpose solvent extractor. The isopropanol of 99.7% purity (Systerm), sulphuric acid of 98% (Fisher Scientific), phenolphthalein of 1% (Systerm) and potassium hydroxide of 99% purity (Systerm) were used for the FFA pre-treatment. The acidic pre-treatment process was aimed to decrease the FFA percentage of the biodiesel feedstock. The raw *J. curcas* triglycerides used in this experimental work contained 20.6% of FFA. The esterified *J. curcas* triglycerides have about 0.6% of the FFA content. Meanwhile, sodium methoxide (Systerm) was utilized as the catalyst in transesterification reaction, and methanol of 99.8% purity (R&M Chemicals) was used for both esterification and transesterification. Ethanol of 99.5% purity (Systerm) was only used for transesterification. Ethyl acetate and N,O-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) were from Fluka for sample preparation. In this study, the percentage of the catalyst loading for the entire experiments was fixed at 1.0% w/w, whereas, the alcohol to triglycerides molar ratio was varied from 4:1 until 7:1. Experiments were conducted using the following equipments; batch reactor, separator funnel, burette and other related glass ware.

### *The Pre-treatment of* Jatropha curcas *Triglycerides*

In this study, the pre-treatment step was carried out to reduce the FFA content of the *Jatropha curcas* oil (triglycerides) to below 1% (w/w). Firstly, the *J. curcas* oil was poured into the reactor and heated. The solution of sulphuric acid in methanol at concentrations 1.0% w/w was heated at 60 °C, and then added to the reactor containing the heated oil. The ratio of methanol to *J. curcas* oil was 60% w/w and the time taken for the pre-treatment was 180 minutes. After the reaction was completed, the mixture was allowed to settle down for 2 h and the methanol water fraction at the top layer was removed. The feedstock with the lowest acid value was then utilized in the subsequent transesterification reaction to produce biodiesel (Azhari *et al*., 2008).

### *Experimental Procedure*

The reactor was initially charged with the desired amount of feedstock (50 g) and heated to 65 ºC using a water bath under constant temperature (*Fig. 2*). The mixture of alcohol (methanol or ethanol) and catalyst was then added to the reactor at which the reaction was assumed to commence. The unreacted alcohol and catalyst were removed via washing process. The complete biodiesel production process is illustrated in *Fig. 1*.

### *Analytical Methods*

The FFA percentage of the feedstock was analyzed using acid based titration technique with 0.1 N of alkali as the standard solution. 2.5 g of *J. curcas* oil was weighed for the analysis after which the

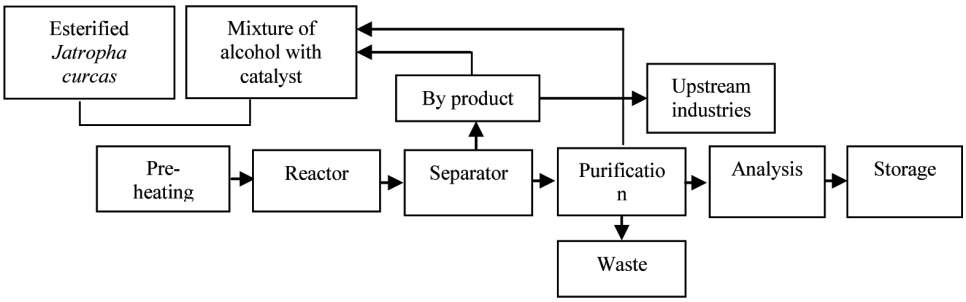


*Fig. 1: Schematic of biodiesel production process*

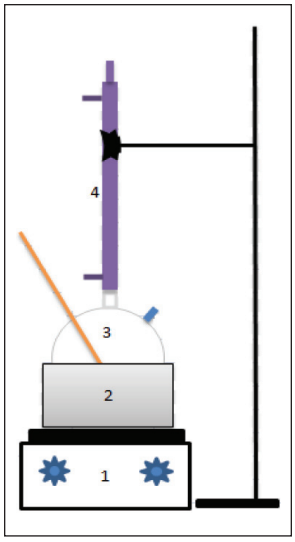


*Fig. 2: Schematic of reactor configuration; (1) Heater c/w stirrer, (2) Water bath, (3) Batch reactor, and (4) Graham condenser*

neutralized solvent was added into the sample. The sample was then shaken gently while titrating with the standard solution until the first permanent colour appeared (Lin *et al*., 1995).

The analysis of the products was conducted using gas chromatography (Agilent 6890 Series), with capillary column SGE 12m × 0.53mm, 0.15µm ID column HT5 (SGE, Australia, Pty. Ltd.), with hydrogen at 26.7 ml/min as a carrier gas and a split ratio of 1:1. The oven temperature was set at an initial temperature of 80 °C, held for 3 minutes, increased from 6°C/min to 340 °C and held for 6 more minutes. The injector and detector temperatures were 300 °C and 360 °C, respectively (Yunus *et al*., 2002).

## RESULTS AND DISCUSSION

### *The Effects of Alcohol Molar Ratio and Temperature*

In this experimental work, the initial content of FFA in *Jatropha curcas* triglycerides was 20.6 %. After the pre-treatment step, it was reduced to an acceptable level (less than 1.0%) prior to

transesterification reaction. This stage was conducted via esterification of *J. curcas* triglycerides with alcohol and mineral acid as the catalyst.

The effect of alcohol molar ratio on *J. curcas* oil (triglycerides) (JCO) plays a significant role on the yield of alkyl esters (biodiesel). In this reaction, the alcohol derivatives chosen for the study were methanol and ethanol. The reaction stoichiometry of *J. curcas* triglycerides requires three moles of alcohol to react with one mole of triglycerides to yield three moles of fatty acid alkyl esters and one mole of glycerine. Based on the thermodynamic equilibrium, a large excess of alcohol is required to force the reaction to the right so that it will be in favour of biodiesel production. Based on the yield of the product, the maximum molar ratio employed in this experimental work was seven folds. The effects of methanol to the JCO molar ratio on the yield of methyl esters formed from alcoholysis were investigated at various amounts of excess methanol and reaction temperatures (see *Fig. 3*).

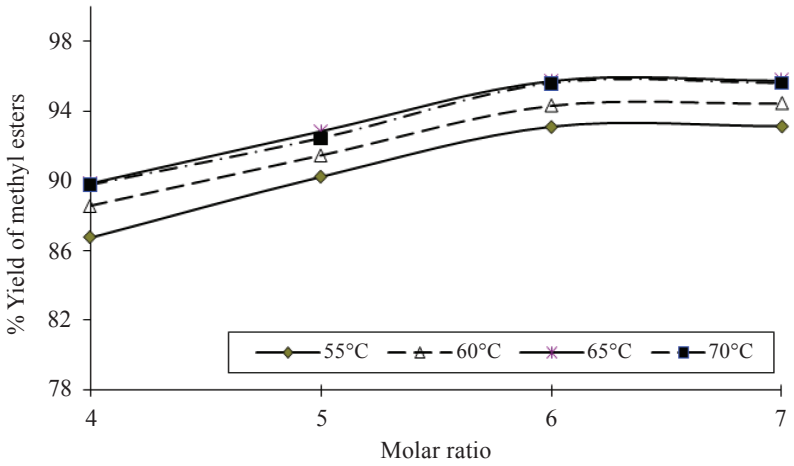


*Fig. 3: The effect of methanol to JCO molar ratio at various temperatures (catalyst loading at 1% w/w)*

The maximum reaction yield at all the temperatures is achieved at a molar ratio of 6:1, as shown in *Fig. 3* and *4*. At lower molar ratios, an incomplete conversion is apparent since the percentage yield of *J. curcas* triglycerides is only 86.7% for the reaction using methanol, while the lowest yield was recorded at 80% for the ethanol. This indicates that a higher molar ratio of the excess reactant to *J. curcas* triglycerides has resulted in a better transesterification reaction until it reaches the optimum value at 6:1 molar ratio for both the alcohol derivatives. Since the transesterification process is a reversible reaction, the increase in the amount of alcohol will shift the reaction to the right, and this further promotes a formation of alkyl esters. The use of excess reactant results in a significant improvement on the product yield. The highest product yield was recorded at 96% using methanol and this was 90% using ethanol (see *Fig. 4*). This could be due to the difference in the molecular structure of methanol and ethanol. In more specific, the two carbon chains in the hydrocarbon structure of ethanol have caused more energy and time to be required to form ethoxide ion as compared to methanol which possesses a single carbon chain. In a similar study by Tapanes *et al*. (2008), a slower reaction rate was reported using ethanol as an excess reactant compared to methanol.

*Fig. 3* and *4* also show that the optimum temperatures for the transesterification reactions for methanol and ethanol are 65°C and 75°C, respectively. Above these temperatures, the reactions are no longer effective because of the boiling point constraints of these alcohols.

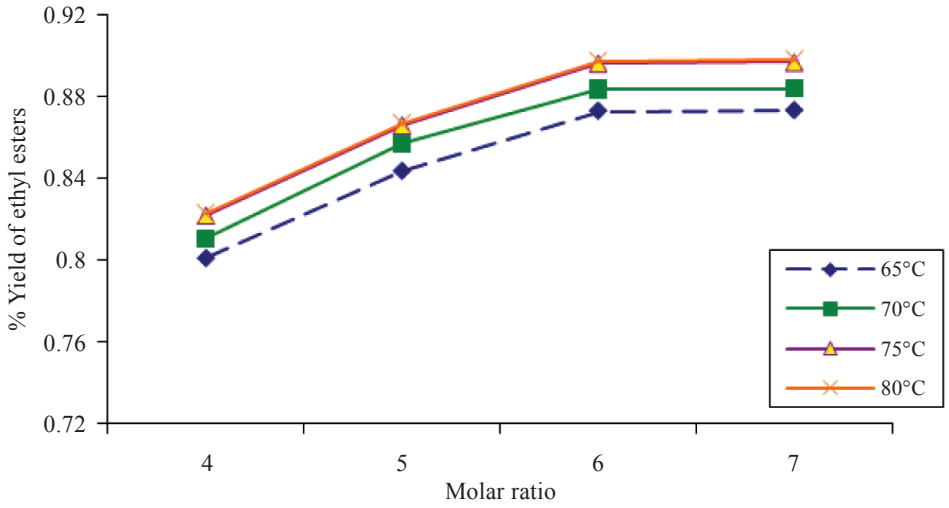


*Fig. 4: The effect of ethanol to JCO molar ratio at various temperatures (catalyst loading at 1% w/w)*

*The Effect of Reaction Time*

*Fig. 5* shows the progress of transesterification reaction at various operating temperatures. The reaction was slow during the early part of the reaction due to the time taken for the mixing and dispersion of alcohol into *J. curcas* oil. However, the reaction progressed rapidly after 20 min until the equilibrium was reached at about 40 min of reaction. This phenomenon demonstrates the reaction pathways which take place during the step wise transesterification process to produce biodiesel. There have not been many discussions done on reaction pathways using sodium methoxide catalyst. However, Freedman *et al*. (1984) reported that the reactions of soybean and sunflower triglycerides with the methoxide catalyst were very fast at the initial part of the reaction. Other researchers have also reported that the difference between the reaction rates should be in the pre-step, where the alkoxide is formed. Figure 5 also shows that since ethoxide is stronger than methoxide, the formation of methoxide ion is easier than ethoxide ion (Tapanes *et al*., 2008), and thus, producing a higher product yield.

The effect of temperature was also examined and is shown in *Fig. 5*. As discussed earlier, the biodiesel yield is affected by the reaction temperature. Since the reaction is endothermic, high temperature increases the rate of reaction. Although the curves show that the rate of reaction increases with temperature, the properties of the alcohol limit the maximum temperature allowable for the reaction. Above its boiling point, the alcohol will vaporize and thus, a disequilibrium condition takes place and thus results in a lower rate of reaction. In this study, the optimum reaction temperature is 65°C for methanol and this is 75°C for ethanol.

*The Properties of Jatropha curcas Biodiesel*

According to Kinast (2003), the potential of methyl and ethyl esters as biodiesel feedstocks is dependent on its quality and must be comparable to the biodiesel standards of certain countries. The properties which define the quality of biodiesel are also used for mineral oil based diesel fuel. Since biodiesel can be produced from vegetable oil of varying origins and quality, it is necessary to have a fuel quality standard to guarantee engine performance and also as a prerequisite for a

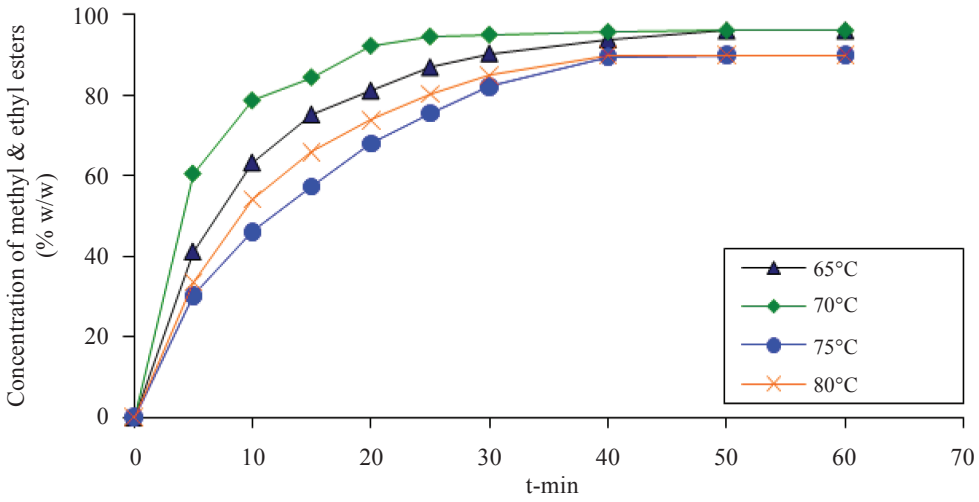


*Fig. 5: The effect of reaction time on the concentration of* Jatropha curcas *methyl and ethyl esters at various temperatures (amount of catalyst loading is 1% w/w)*

successful market penetration of biodiesel (Srivastava & Prasad, 2000; Meher *et al*., 2004). Table 2 presents the properties of the *J. curcas*-based biodiesel and a comparison to the characteristics of fossil-based diesel fuel.

In this study, the physical properties of *J. curcas* alkyl esters, such as kinematics viscosity, density, flash point, pour point, cloud point, moisture content, iodine value, calorific value and acid number, were analyzed. The results show that the calorific value of *J. curcas* ethyl esters is comparable to that of the fossil diesel fuel. In addition, the flash point is higher than the diesel fuel. Although the iodine value of *J. curcas* alkyl esters is nearly comparable to that of the diesel fuel, the pour point and cloud point are slightly higher. In terms of viscosity, which controls the fuel injection, the biodiesel shows fairly higher values compared to the diesel fuel. This is good for engine lubrication. In correlation with ignition method, the flash point indicates the temperature

TABLE 2
The physical properties of *Jatropha curcas* alkyl esters and their comparison to the characteristics of diesel fuel (Sources: [d]Pramanik, 2003; [e]Puhan *et al*., 2005; [f]Ali & Hanna, 1994; [g]Ikwuagwu *et al*., 2000; [h]Altin *et al*., 2001).

| No | Properties | JME* | JEE* | FDF* |
|---|---|---|---|---|
| 1 | Density (g/cc), 30ºC | 0.865 | 0.889 | 0.836-0.850[d] |
| 2 | Kinematics viscosity (cSt) | 4.33 | 5.46 | 2.4[e] |
| 3 | Moisture content (%) | 0.16 | 0.17 | <0.05[f] |
| 4 | Pour point, ºC | -15 | -10 | -33[f] |
| 5 | Cloud point, ºC | -9 | -4 | -15[e] |
| 6 | Flash point, ºC | 176 | 181 | 60[d] |
| 7 | Iodine value | 99 | 107 | 84[g] |
| 8 | Calorific value, MJ/Kg | 38.72 | 40.96 | 43[h] |
| 9 | Acid number | 0.14 | 0.56 | 0.02[g] |

* JME = *Jatropha curcas* methyl esters, JEE = *Jatropha curcas* ethyl esters, FDF = Fossil-based diesel fuel

above which the fuel will ignite when exposed to a spark (Thompson *et al*., 1998). The flash points for both biodiesels are higher than the diesel; thus, they are generally safer but most likely require special ignition devise for start up.

In a similar study, Knothe *et al*. (1996) reported that the neat vegetable oil and its methyl esters have nearly identical iodine values. As a result, biodiesel from vegetable oil with high content of unsaturated fatty acid compounds will have low pour point and cloud point. This degree unsaturation was selected as an important criterion for fatty acid alkyl esters. Furthermore, Azam *et al*. (2005) reported other significant characteristics which include kinematics viscosity, flash point, moisture content and acid number. Acid number is due to oxidative degradation of the substance. A few reports also highlighted that the oxidative degradation develops from the hydroperoxide toward secondary oxidation products. It is influenced by the nature of the original fatty substance (in terms of the number of double bounds) and its quality with particular reference to the presences of hydroperoxides, natural antioxidants, pro-oxidizing agents, as well as air and high temperature condition.

## CONCLUSION

The alcoholysis of *Jatropha curcas* triglycerides in the presence of sodium methoxide catalyst using ethanol and methanol as the excess reactants was studied. The results have shown that the rate of reaction and product yield are affected by the molar ratio of alcohol to *JCO*, reaction time and reaction temperature. Meanwhile, the difference in the molecular structure of the alcohols affects the product yield. The optimum operating conditions were molar ratio of alcohol to JCO at 6:1 and the optimum reaction time at 50 min. The highest percentage yield of product for methanol was achieved at 96%, whereas the highest product yield was 90% with ethanol. The properties of the *J. curcas*-based biodiesels were analysed and found to be comparable to that of the fossil-based diesel fuel.

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