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Determination of deep eutectic solvents as eco-friendly catalysts for biodiesel esterification from an alcohol-palmitic acid mixture

Yu Ri Lee, Yu Jin Lee, Wanwan Ma, and Kyung Ho Row†

Department of Chemistry and Chemical Engineering, Inha University, Incheon 22212, Korea
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Abstract−Deep eutectic solvents (DESs) were prepared by mixing a quaternary salt as a hydrogen bond acceptor with a hydrogen bond donor. In this study, DESs had an excellent effect as a solvent-catalyst for the esterification of palmitic acid and methanol. This method was found to be safe, mild, simple, and eco-friendly. A range of DESs with different mixing ratios were used to optimize the preparation of methyl palmitate. Other factors, such as temperature, time and DESs/methanol ratio, were also examined. The optimal DES was prepared from tetrabutyl ammonium chloride and acetic acid (1 : 2); the methanol and palmitic acid sample to DES ratio was 1 : 0.5 (v/v). The reaction was optimized at a methanol/palmitic acid ratio of 10 : 1 (mol/mol) at 60 °C for 60 min. The yield was 94.3% under the optimized conditions. Therefore, DESs can be developed as a catalyst for the esterification of palmitic acid for obtaining methyl palmitate as biodiesel, and have potential applicability in other biodiesel pretreatments.

Keywords: Deep Eutectic Solvents, Biodiesel, Methyl Palmitate, Esterification

INTRODUCTION

Biodiesel has attracted increasing attention because of its environmental benefits and that it is made from renewable resources [1]. Owing to the increases in crude oil prices, limited feedstock of fossil oil and environmental concerns, vegetable oils, such as corn [2], soybean and palm oil [3,4], and animal fats, have attracted renewed interest in the production of biodiesel fuels [5]. Fats and oils are commonly water-insoluble, hydrophobic substances in plants and animals that are made up of one mole of glycerol and three moles of fatty acids, and are generally referred to as triglycerides [6]. Fatty acids differ according to the carbon chain length and number of double bonds. Biodiesel is a renewable, alternative diesel fuel of a domestic origin derived from a variety of fats and oils from a transesterification reaction. Accordingly, it is composed of alkyl esters, normally methyl esters of the fatty acids of the parent oil or fat [7].

DESs are non-toxic, have low reactivity with water and are prepared easily at low cost. Most importantly, they are biodegradable [8,9]. DESs are formed by mixing two or more components, such as a variety of quaternary ammonium salts and carboxylic acids. Therefore, they have a lower melting point than their component compounds. The physical properties of DESs are affected considerably by the structure of the carboxylic acid. On the other hand, the phase behavior of these mixtures can be modeled simply by considering the mole fraction of the carboxylic acid in the mixture [10]. DESs are also generated from organic halide salts with organic compounds, which are hydrogen bond donors (HBDs). Charge delocalization is achieved through an HBD between the halide anion and the amide moiety. A eutectic mixture of choline chloride (ChCl) with urea produces a liquid with a low melting point. This liquid has interesting solvent properties similar to ambient temperature ionic liquids, which are called "green" solvents, Moreover, a wide range of solutes have been found to exhibit high solubility [11]. Based on this characteristic, the potential of DES as synthesis catalysts for biodiesel preparation via DES-based extraction from natural products has been reported [12-15]. Generally, DESs are used in the separation of glycerol from biodiesel because of their high polarity. Biodiesel is produced by a transesterification reaction of oil with methanol. After the reaction, the removal of glycerol from biodiesel is important because the quality of biodiesel is determined by the concentration of glycerol [16,17]. In this context, Ott *et al.* removed the waste glycerol from acid-catalyzed biodiesel by adding choline chloride, which forms a DES with waste glycerol [18]. In addition, DESs have been used as potential catalysts for the esterification of biodiesel [19]. Chen et al. synthesized biodiesel using choline chloride and zinc chloride-based DESs as a Lewis acidic catalyst from soybean oil [20].

In this study, DESs were assessed as eco-friendly catalysts for biodiesel esterification. Methyl palmitate was synthesized from palmitic acids. The individual fatty acid methyl ester itself was evaluated for its stability against exposure to methanol under a variety of exposure conditions. A range of DESs with different mixing ratios were used to optimize the preparation of methyl palmitate. Other factors, such as temperature, time, methanol/palmitic acid ratio, and sample/DESs ratio were also examined systematically, and the level of methyl palmitate production was determined by gas chromatography (GC).

EXPERIMENTAL

1. Materials

Choline chloride (>98.0%), tetramethyl ammonium chloride

†To whom correspondence should be addressed.
E-mail: rowkho@inha.ac.kr

Table 1. Compositions of the synthesized DESs

Abbreviation	Salt	HBD	Salt/HBD ratio	Ref.
DES-1	Choline Chloride	Urea	1 : 2	[16]
DES-2	Choline Chloride	Ethylene glycol	1 : 2	[16]
DES-3	Choline Chloride	Glycerol	1 : 2	[31]
DES-4	Choline Chloride	Malonic acid	1 : 1	[31]
DES-5	Choline Chloride	Lactic acid	1 : 1	[31]
DES-6	Tetramethyl ammonium chloride	Oxalic acid	1 : 2	[32]
DES-7	Tetrabuthyl ammonium chloride	Acetic acid	1 : 2	[33]
DES-8	Lactic acid	D-(+)-Glucose	5 : 1	[31]

(>98.0%), tetrabutyl ammonium chloride (>98.0%), ethylene glycol (>99.5%), methyl palmitate (>97.0%), were purchased from Tokyo Chemical Industry Co. Methanol (>99.9%) and acetic acid (>98.0%) were acquired from Duksan Pure Chemicals Co., Ltd. (Ansan, Korea). Urea (>98.0%), palmitic acid (>98.0%), oxalic acid (>98.0%), lactic acid, malonic acid, and D-(+)-glucose were acquired from Sigma-Aldrich (St. Louis, MO, USA) Glycerol (>99.0%) was supplied by Duksan Pure Chemicals Co., Ltd. (Ansan, Korea).

2. Preparation of DESs

The DESs were prepared by heating the salt and a hydrogen bond donor (HBD) at a set ratio at 60 °C for 60 min with constant stirring until a homogeneous liquid formed [21]. Table 1 lists the compositions of the synthesized DESs.

3. Preparation of Standard Solution and Sample for Esterification Reaction

To obtain the standard curves, 2 μL of a solution that contained an accurate concentration of methyl palmitate (0.001, 0.025, 0.1, 0.25, 0.50, 0.75, 1.00, 1.50, and 2.00 mg/ml) in methanol, was injected into a gas chromatograph. To prepare the sample solution, methanol and palmitic acid (100 : 1, 50 : 1, 10 : 1, 5 : 1 and 2 : 1, mol/mol) and the DESs were placed into a flask. The mixture was then stirred at 60 °C for 60 min for different times, and the temperature and reaction ratio were varied. After the reaction, the mixture was analyzed by GC.

4. Gas Chromatography Analysis

GC was conducted on a Yong Lin Instrument (Korea) GC-6100 equipped with a DB-1701 capillary column (30 m×0.320 mm×1.00 μm) (Agilent Technologies) and detected using a flame ionization detector. The carrier gas used was nitrogen with a flow rate of 1.8 mL/min. The GC injection temperature was 280 °C and the detector temperature was 300 °C. The temperature program of the oven was increased from 60 °C to 140 °C at a rate of 5 °C /min and then increased to 220 °C at a rate of 10 °C/min. Finally, the temperature was increased to 280 °C over a 4 min period.

RESULTS AND DISCUSSION

1. Linearity and Reproducibility

A standard solution of methyl palmitate with methanol was injected into a gas chromatograph to obtain the standard curve. As a result, a linear regression equation, Y=595.97x+123.17 (r^2=0.9993), was obtained. Assays of the repeatability were calculated as the relative standard deviations (RSDs) by injecting the standard solutions 5 times over a five-day period. RSDs less than 4.15% revealed acceptable precision and accuracy (Table 2).

2. Mechanism of Transesterification

The transesterification process is catalyzed by Brønsted acid, such as sulfonic acid, sulfuric acid and hydrochloric acid, and gives a high biodiesel yield but the reaction time is long [22]. Therefore, DESs was used to overcome the problems with organic acid catalysis, such as pollution and long reaction times. Fig. 1 shows the reaction mechanism of transesterification. DESs are formed by mixing two or more components, such as quaternary salts and HBD. The salt, such as tetramethyl ammonium chloride, is catalyzed mainly

Table 2. Intra-day and inter-day precision, accuracy and recovery of methyl palmitate with three different concentrations

	Concentration/ (μg/mL)	Intra-day		Inter-day		Method recovery/%
		Measured concentration/ (μg/mL)	Precision RSD/%	Measured concentration/ (μg/mL)	Precision RSD/%	
Methyl palmitate	1	1.23 (±0.25)	4.15 (±3.85)	1.14 (±2.11)	3.06 (±1.98)	99.8
	25	25.18 (±1.22)	3.32 (±2.18)	25.11 (±0.38)	1.82 (±0.14)	99.2
	100	99.85 (±0.48)	3.12 (±3.12)	99.52 (±1.34)	2.15 (±1.68)	99.5
	250	249.48 (±0.52)	2.34 (±2.41)	251.46 (±1.46)	0.98 (±1.43)	98.9
	500	500.64 (±0.64)	1.67 (±1.72)	501.67 (±1.67)	1.64 (±2.32)	99.1
	750	751.02 (±1.02)	2.04 (±2.05)	752.17 (±2.17)	1.78 (±2.07)	98.4
	1000	998.94 (±1.06)	3.94 (±3.71)	1001.10 (±1.10)	2.67 (±0.75)	99.2
	1500	1499.76 (±0.24)	4.04 (±2.62)	1500.64 (±0.64)	3.11 (±0.86)	99.7
	2000	2001.23 (±1.23)	1.71 (±2.34)	1998.84 (±1.16)	2.48 (±1.61)	98.9

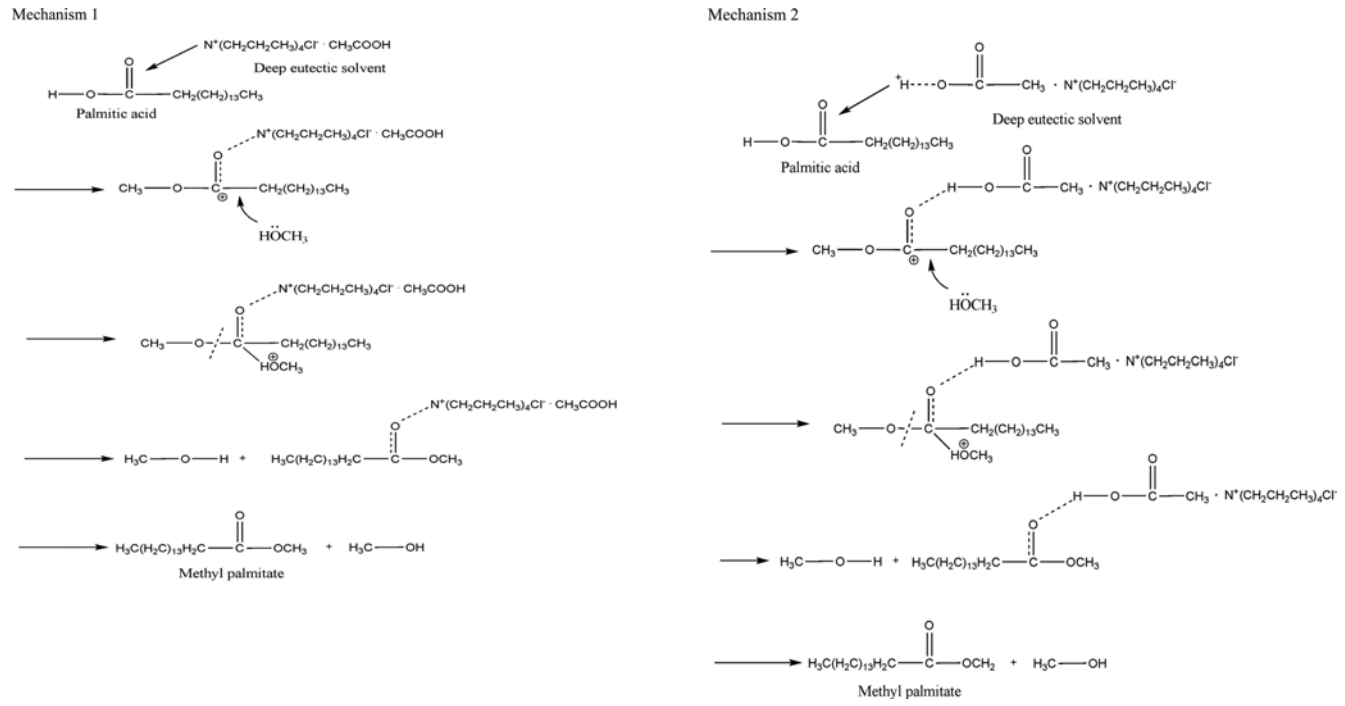

Fig. 1. Transesterification reaction mechanism of palmitic acid and methanol with DESs as catalysis.

by the salt of DESs according to mechanism 1. The ammonium ion of the DESs is deprotonated and the proton is transferred from DESs to the oxygen on the carbonyl group of palmitic acid. Palmitic acid promotes the successive attack of methanol as a nucleophilic reagent. As a result, the bond between carbonyl carbon and the oxygen of the methanol framework is split simultaneously with bond formation between the carbonyl carbon and oxygen of the hydroxyl group linked to methanol. As result, the formation of methyl palmitate and methanol [23,24]. In mechanism 2, the acetic acid of the DESs was deprotonated and the proton was transferred from DESs to the oxygen on the carbonyl group of palmitic acid. The DESs catalyst is expected to undergo these two mechanisms. Therefore, DESs catalysis can increase the yield and reduce the environmental pollution.

3. Selection of DESs

The DESs were selected to catalyze the synthesis of biodiesel. DES-1, DES-2 and DES-3 have no acid HBD and could promote the esterification reaction because biodiesel is typically produced by the alkali- or acid-catalyzed esterification of triglyceride. Normally, sulfuric, phosphoric, hydrochloric, and organic sulfonic acid are used as the acid catalysts for esterification. The organic acidic catalysts are toxic and cause environmental pollution [25]. In addi-

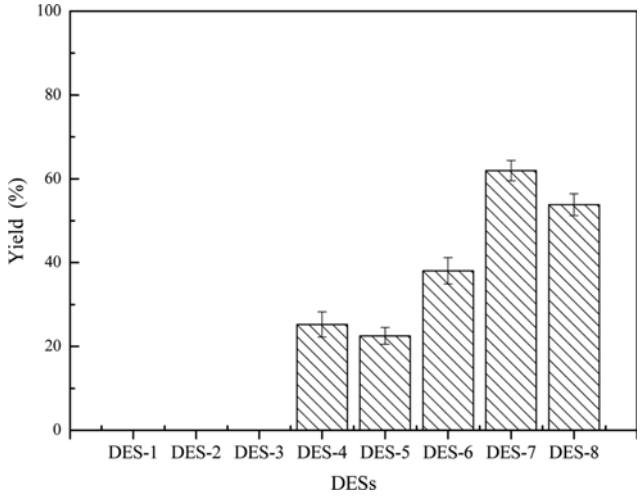

Fig. 2. Effect of DESs on the synthesis of methyl palmitate (Methanol/palmitic acid: 10 : 1 (mol : mol), sample/DES ratio: 1 : 5 (v/v), temperature: 60 °C, time: 60 min).

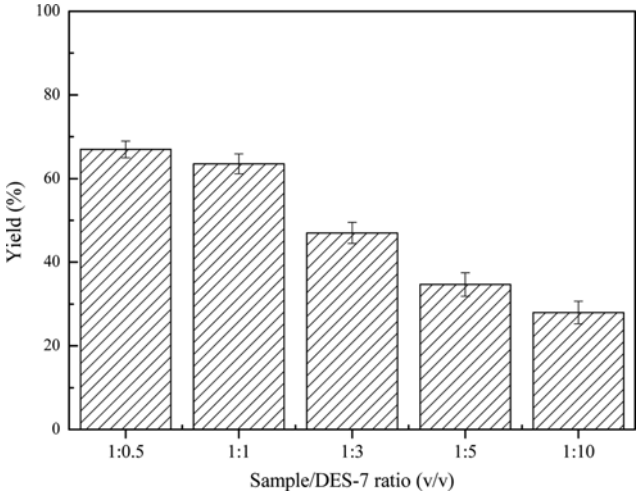

Fig. 3. Effect of the palmitic acid and methanol mixture to DES ratio (Methanol/palmitic acid: 10 : 1 (mol : mol), temperature: 60 °C, time: 60 min).

tion, an ionic liquid was used as a catalyst for the esterification reaction. On the other hand, acidic-ionic liquids have some problems, such as high synthesis cost and a difficult synthesis process [26]. Therefore, this study selected DESs as the eco-friendly catalysts for the esterification reaction of palmitic acid. Fig. 2 shows the effects of different DESs on the esterification reaction. The yield was only 61.9% when DES-7 was used a catalyst.

4. Optimization of the Sample to DES Ratio

Fig. 3 shows the effects of the sample and DESs ratio. The sample and DESs ratio was 1 : 0.5, 1 : 1, 1 : 3, 1 : 5, and 1 : 10 to optimize the reaction conditions. The yield was relatively constant at 1 : 0.5 and 1 : 1, but was lower at 1 : 3, 1 : 5 and 1 : 10. This shows that the optimal sample to DESs ratio is 1 : 0.5. Under the above conditions, the highest yield was 67.0%. DESs have a lower reaction effect because of their high viscosity. Therefore, the addition of a reaction sample to DESs to reduce the viscosity can be a considerable advantage.

5. Optimization of Methanol and Palmitic Acid Ratio

The methanol and palmitic acid ratio is one of the main conditions for the reaction. Some studies suggested that a methanol-to-fatty acid ratio of 3 : 1 increased the production of fatty acid methyl esters, which then decreased when the methanol concentration was increased further [27]. Fig. 4 shows the effects of the methanol/palmitic acid sample ratio. In this experiment, the reaction temperature and time were fixed to 60 °C and 60 min, respectively. The methanol-to-palmitic acid sample ratio was varied (100 : 1, 50 : 1, 10 : 1, 5 : 1, and 2 : 1). The yields were higher at 100 : 1, 50 : 1, 10 : 1, and 5 : 1, but the yields were lower at 2 : 1 (Fig. 3). Therefore, the optimal methanol and palmitic acid ratio was found to be 10 : 1 (mol : mol).

6. Optimization of Reaction Temperature

Normally, temperature is one of the key factors for an effective catalyst in a reaction. Although the reaction rates increase with increasing temperature, a high temperature might have a reverse effect because of the vaporization of methanol in the esterification reaction. In this study, the sample ratio was fixed to 10 : 1. Fig. 5 shows the effects of temperature on the yield in the esterification reaction.

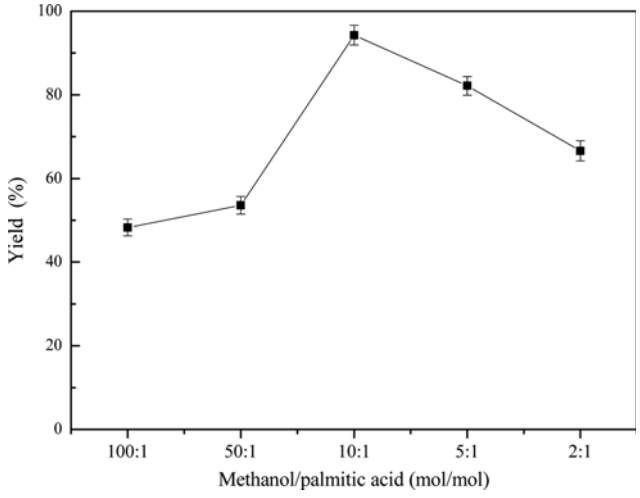

Fig. 4. Effect of the methanol to palmitic acid ratio (Sample/DES-7 ratio: 1 : 0.5 (v/v), temperature: 60 °C, time: 60 min).

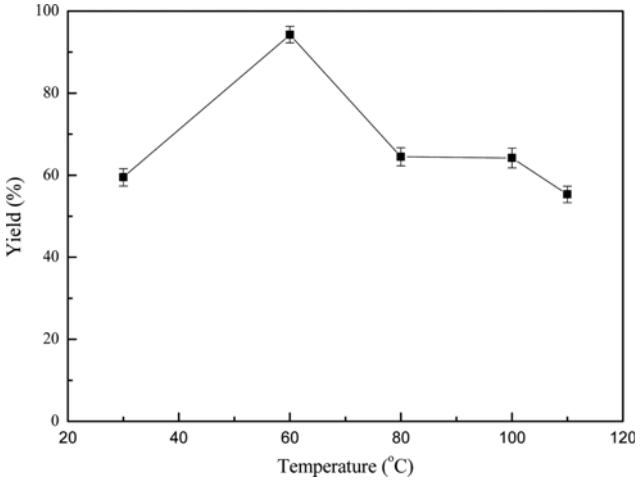

Fig. 5. Effect of temperature on the synthesis of methyl palmitate (Methanol/palmitic acid: 10 : 1 (mol : mol), sample/DES-7 ratio: 1 : 0.5 (v/v), time: 60 min).

The reaction temperature was in the range, 30-110 °C. The yield increased from 30 °C to 60 °C, and decreased with further increases in temperature. These results show that a higher temperature is not an advantage for the reaction. Therefore, an optimal temperature of 60 °C was selected for the esterification reaction to minimize the energy use. Leung et al. reported the optimal transesterification reaction condition for biodiesel product from neat vegetable oil and waste recycled oils using sodium hydroxide, potassium hydroxide and sodium methoxide as alkaline catalysts. The optimal reaction temperature was 60 °C, and used frying oil containing 20.4% palmitic acid was used [28].

7. Optimization of Reaction Time

The reaction time is an important variable in kinetics studies and the design of reactors. In addition, it is a crucial factor in the process and range of chemical reactions. Fig. 6 shows the effects of the reaction time. The reaction temperature was fixed to 60 °C and

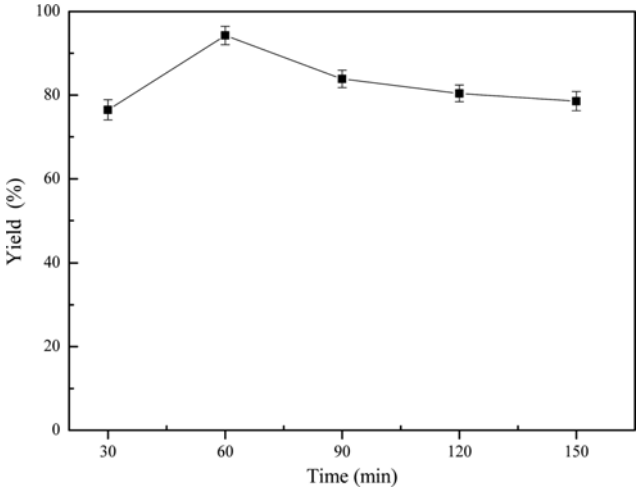

Fig. 6. Effect of time on the synthesis of methyl palmitate (Methanol/palmitic acid: 10 : 1 (mol : mol), sample/DES-7 ratio: 1 : 0.5 (v/v), temperature: 60 °C).

the sample/DES ratio was fixed to 1 : 0.5 (v/v). The reaction time was varied from 30 to 150 min to optimize the synthesis. The yield increased from 30 to 60 min, but was relatively constant from 60 to 150 min. This shows that the optimal synthesis time is 60 min. Under the above conditions, the highest yield was 94.3%. Some studies selected 60 min as the optimal reaction time for esterification [29]. DESs acidic catalysts are superior to IL acidic catalysts because acidic DESs catalysts can reduce the reaction time. Normally, IL acidic catalysts require several hours for the esterification reaction [30].

CONCLUSION

Ionic liquids are very popular solvents in the bioenergy field because of their unique physical properties. However, they have toxicity issues and low economic efficiency. DESs have been suggested as versatile alternatives. Therefore, in this study, DESs were applied successfully to the pretreatment of biodiesel by the esterification of a palmitic acid and methanol mixture over DESs. The synthesis conditions of the DESs, such as salts, hydrogen bond donors and ratio, were varied to determine the optimal conditions. The reaction conditions, such as the methanol/palmitic acid ratio, sample/DES ratio, time, and temperature, were varied. Under the optimal conditions, the yield was 94.3%. In conclusion, DESs can be developed as catalysts for the esterification of palmitic acid, and have potential applicability to other biodiesel pretreatments.

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