

PROGRESS REPORT

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**THE USE OF THREE PHASE REACTION FOR BIODIESEL
PRODUCTION**

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Objective (s)

- To investigate the performance of a three phase reaction system in the production of biodiesel from animal fats and model mixtures of triglycerides (TGs) and free fatty acids (FFAs) using solid catalysts.
- To compare the performance of acid catalysts under the conditions of three phase reactions and batch reactions.

Project Overview

Biodiesel synthesis from biomass provides an effective way for utilizing more efficiently renewable resources to produce a fuel that can replace petroleum derived diesel, helping in the effort to cut our nation's dependence on imported oil. Currently, fats and oils are treated with alkali homogeneous catalysts (either NaOH or KOH) and a simple alcohol (i.e., MeOH or EtOH) to form monoalkylesters (biodiesel) and glycerol (a by-product) (Ma and Hanna, 1999). However, alkali homogeneous catalysts are expensive to use since the catalyst cannot be recycled for re-utilization (Lotero et al., 2006). Hence, they have to be separated and disposed as waste. In addition, free fatty acids (FFAs) in the feedstock can react with the alkali catalyst, deactivating it and producing soap, affecting overall productivity. Thus, feedstocks have to be refined before use. As an alternative, homogeneous strong acid catalysts can replace alkaline catalysts. Strong homogeneous acids like sulfuric acid can transform both triglycerides (TGs) and FFAs to biodiesel, although with lower activity than alkali catalysts. However, liquid acid catalysts are corrosive and pose environmental problems. On the other hand, use of solid acid catalysts as substitutes for strong liquid acid catalysts would eliminate corrosion and environmental problems associated with liquid acids and could reduce the number of reaction and separation steps required in the conversion of fats and oils to biodiesel, allowing for more economical processing.

Research in our laboratories using solid acids for the reaction of biodiesel model precursor compounds with methanol has shown that solid acids can indeed substitute for strong liquid acids with similar activities on a per site basis (Liu et al., 2006a; Lopez et al., 2005). However, demonstrating the promising activity of solid acids is only the first step to the implementation of newer biomass processing technologies. For instance, contrary to homogeneous catalysts, heterogeneous catalysts may have a complex structure with a network of pores that reactants have to access before reacting. Methanol can preferentially adsorb in the interior of small mesopores, making difficult the access and diffusion of larger non-polar molecules like TGs and FFAs. Hence, a batch reactor system, which uses large amounts of methanol facilitates catalyst pore filling. In addition, water formed during esterification of free fatty acids can also poison acid sites lowering catalyst activity (Liu et al., 2005; Liu et al., 2006a).

To exploit the full potential of heterogeneous catalysts for biomass processing and biodiesel production the use of three phase reaction systems where the catalyst (a solid), the lipid feedstock (a liquid), and a gaseous solution of methanol are reacted was proposed. A three phase reaction system guarantees that TGs and FFAs are at all times in direct contact with catalytic active sites at the solid surface overcoming methanol pore filling problems. In addition, the

temperature range (120-200°C) used with this system allows to obtain higher catalyst activities and simultaneously co-distillate unreacted methanol and water, avoiding the catalyst poison effect of the latter. An important part of this research is that for the first time performance comparisons between three phase reaction systems and batch systems are being conducted for the synthesis of biodiesel, allowing for an initial quantification of overall advantages of using three phase reaction systems. This study has initially used an animal fat –poultry fat- as the lipid feedstock.

Impact and Significance

To be economically viable and to compete commercially with petroleum-based diesel fuel, processes for the synthesis of biodiesel need to involve as few reaction steps as possible and to minimize separation steps (Lotero et al., 2006). This can be accomplished with the use of heterogeneous (solid) catalysts. The use of heterogeneous catalysts for the commercial production of biodiesel has been overlooked because of a lack of research and understanding of the main variables affecting solid catalysts activity for biodiesel forming reactions such as transesterification and esterification. Our research group over the last 3 years has systematically studied the catalysis of biodiesel forming reaction using heterogeneous catalysts (Liu et al., 2005; Liu et al., 2006a; Liu et al., 2006b; Liu et al., 2006c; Lopez et al., 2005; Lotero et al., 2006; Lotero et al., 2005; Suwannakarn et al., 2006a; Suwannakarn et al., 2006b). Based on the understanding of the main variables that affect catalyst activity for solid acids, we present here a novel methodology for the production of biodiesel from animal fats using a three phase reaction instead of the conventional batch type one phase reaction. On the latter, both reagents and catalyst are in the same phase requiring intensive separation steps to reach acceptable product purity standards. Using technology based on a three phase reaction with a solid acid catalyst should give rise to continuous processing methodologies capable to substantially increase production efficiency and volume with only a few-to-none separation steps, lowering the overall biodiesel production cost.

Project Activities

- **Methodology**
 - **Materials**

All experiments use a commercially available catalyst, tungstated zirconia (13.4 wt% W) provided by Magnesium Electron Inc. (MEI, Manchester, UK). Anhydrous methanol (99.9 wt%) was purchased from Aldrich. High grade poultry fat with an acid content of less than 0.2% was kindly provided by Fieldale Farms Corporation. Tripalmitin, dipalmitin, α -monopalmitin, glycerol and methyl palmitate were purchased from Sigma and used as reference compounds for GC calibration. All analytical chemicals were chromatographically pure (99 wt%) and used without further purification. Hexane and ethyl acetate of HPLC grade were obtained from Fisher Scientific. These solvents are mixed with reaction samples in a volume ratio of 1:1. The samples thus prepared are used for GC analysis.

- **Solid Catalyst Pretreatment**

Tungstated zirconia (WZ) was calcined at 700°C for 1 h and stored in a desiccator until use. Prior to reaction the catalyst was pretreated for 3 h in flowing UHP.

- **Catalyst Characterization**

BET surface area (S_{BET}) analyses were conducted for WZ after its calcination. Prior to surface area analysis, the catalyst sample was degassed at 10^{-3} mm Hg for 3 h. Adsorption measurements were carried out using UHP N_2 adsorption at -196°C in a Micromeritics ASAP 2010.

Information about catalyst composition was obtained by elemental analysis using ICP (Galbraith Laboratory, Knoxville, TN).

NH_3 -TPD for characterization of acid site density was carried out using an Altamira AMI-1. A 0.3 g sample of catalyst was heated to 315°C in 30 ml/min of helium for 1 h to remove adsorbed impurities. Next, the sample was cooled to room temperature and saturated for 2 h using 100 ml/min of 10% NH_3/He . The system was flushed for 2 h with helium (30 ml/min) at room temperature and then the temperature was increased to 60 °C at a rate of 2 °C/min where it was held for 4 h to eliminate physisorbed NH_3 . For TPD, the temperature was increased to 600 °C at a rate of 10 °C/min. A TCD detector was used to measure the NH_3 desorption profile. A blank study of the TPD ramp was obtained in order to account for the catalyst desorption background.

Monochromatic powder X-ray diffractograms were recorded in the 5° to 90° 2θ range for WZ using a XDS 2000 (Scintag Inc.) instrument. The diffractometer used $\text{Cu K}\alpha$ radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$.

- **Reaction Studies**

- **Reaction Systems**

For benchmarking purposes, transesterification of poultry fat with methanol has been carried out at 120°C in a Parr 4590 batch reactor consisting of a stainless steel chamber, a glass liner, a three-blade impeller and, a thermocouple. The molar ratio of methanol to poultry fat was 30:1. The catalyst concentration was 10 wt% based on the poultry fat weight.

The three phase reaction studies involve first the construction of a suitable three phase reactor system, which is now in its final stage. A complete description of the three phase reactor system is given in the results section below. By early October 2006 the three phase reaction reactor should be completed and ready to operate.

- **Method of Analysis**

A 0.15 ml sample is periodically extracted from the reaction mixture using a microscale syringe with a pressure-lock button. The reaction sample was immediately mixed with 0.8 ml solvent followed by centrifuging to separate catalyst particles. 40 μ L of homogeneous liquid was then withdrawn and further diluted in 5 ml solvent containing a known amount of methyl laurate, an internal standard, followed by GC analysis.

GC analysis is performed using a Hewlett-Packard 6890 gas chromatograph equipped with an automatic injector, an on-column inlet, a 15 m x 0.25 mm x 0.1 μ m BPX5 column and a FID detector. Following the injection of 1 μ L analyte, the column temperature is initially held at 50°C for 1 min, then ramped up at 15°C/min to 370°C and maintained there for 4 min. UHP helium is used as the carrier gas flowing at a constant rate of 6.0 ml/min.

- **Results**

- **Catalyst Characterization**

XRD showed the tetragonal structure for the zirconium oxide present in WZ calcined at 700°C. No XRD signals were observed for the formation of WO_x crystallites. Table 1 provides BET, composition, and TPD results for WZ.

Table 1: WZ characterization.

S_{BET} (m^2/g)	Elemental analysis (wt %)	Site concentration (μmol/g)
89.2 \pm 1.4	13.42% (W)	54

- **Reaction Chemistry**

Transesterification of TGs with alcohols proceeds via 3 consecutive and reversible reactions where the FFA moieties combine with the alcohol to produce a fatty acid alkyl ester, di- and monoglyceride intermediates, and finally a glycerol by-product. Figure 1 shows the reactions involved in the transesterification of a TG with methanol. The stoichiometric reaction requires one mole of TG and 3 moles of methanol to produce 3 moles of biodiesel and 1 mole of glycerol.

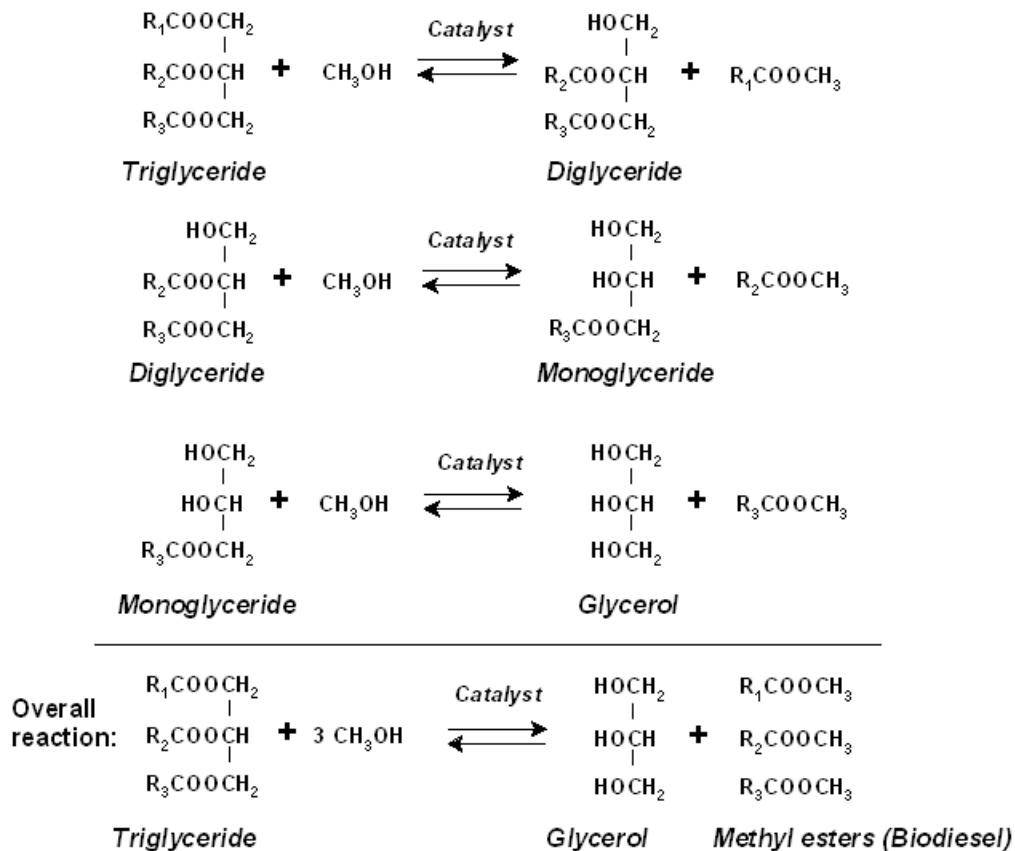


Figure 1: Transesterification reactions of a TG with methanol.

o Catalyst Activity under Batch Processing Conditions

The initial molar ratio of methanol-to-TG used was 30:1. The high methanol-to-TG molar ratio is required due to the slower reaction rate observed for acid catalyzed transesterification compared to the base catalyzed reaction (Mittelbach et al., 1996; Siler-Marinkovic and Tomasevich, 1998). WZ showed very low activity when used in a batch reaction with methanol and the lipid reagents in the same phase at 120°C (Figure 2). Since WZ has site acidity very close to sulfuric acid's (Lopez et al., 2005), and given that sulfuric acid has been successfully used for TG transesterification at temperatures as low as 80°C, the low catalytic activity of WZ for poultry fat transesterification most probably was due to catalyst pore filling by methanol. Methanol pore filling can surely block the diffusion and access of larger non-polar molecules like TGs to catalytic acid sites, inhibiting the reaction.

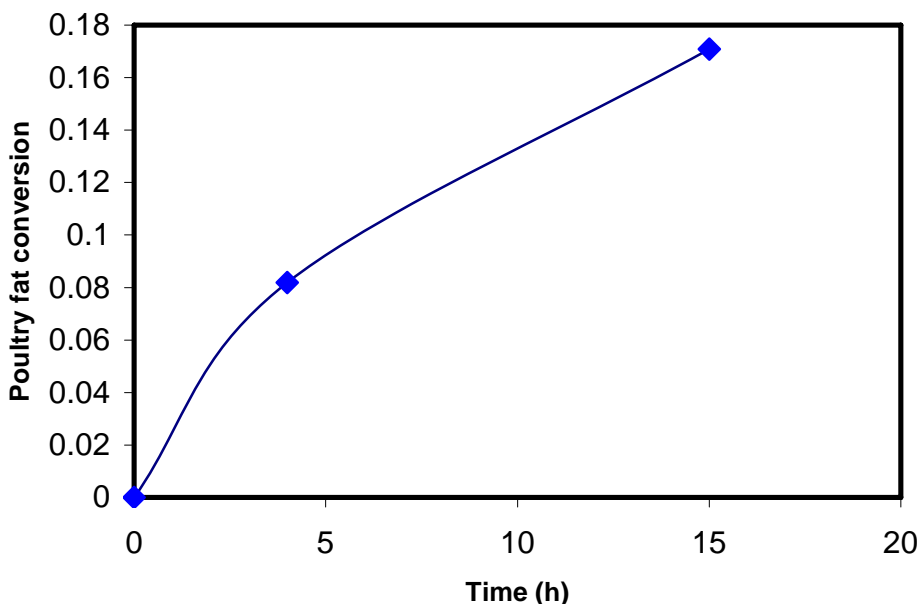


Figure 2: Conversion profile for the transesterification of poultry fat (PF) with methanol using WZ as the catalyst (reaction conditions: methanol:PF = 30, T = 120°C, catalyst concentration = 10 wt.% based on the TG weight).

o **Construction of a Three Phase Reaction System**

A schematic representation of the three phase reaction system under construction at Clemson is shown below in Figure 3.

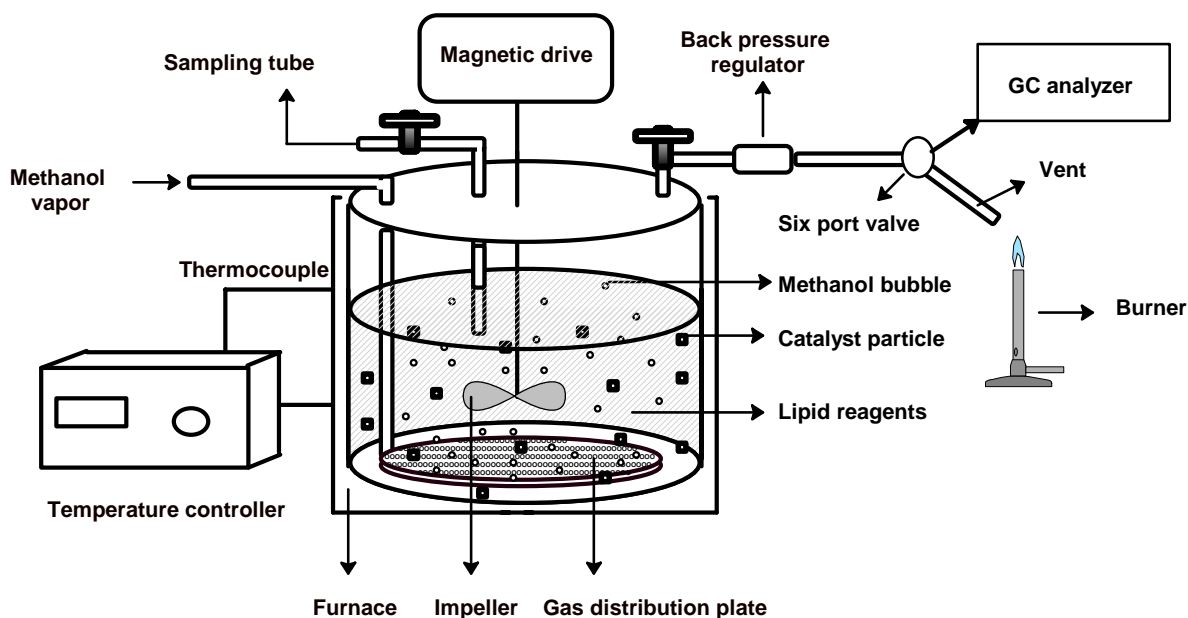


Figure 3: Schematic representation of a semi-batch three phase reaction system.

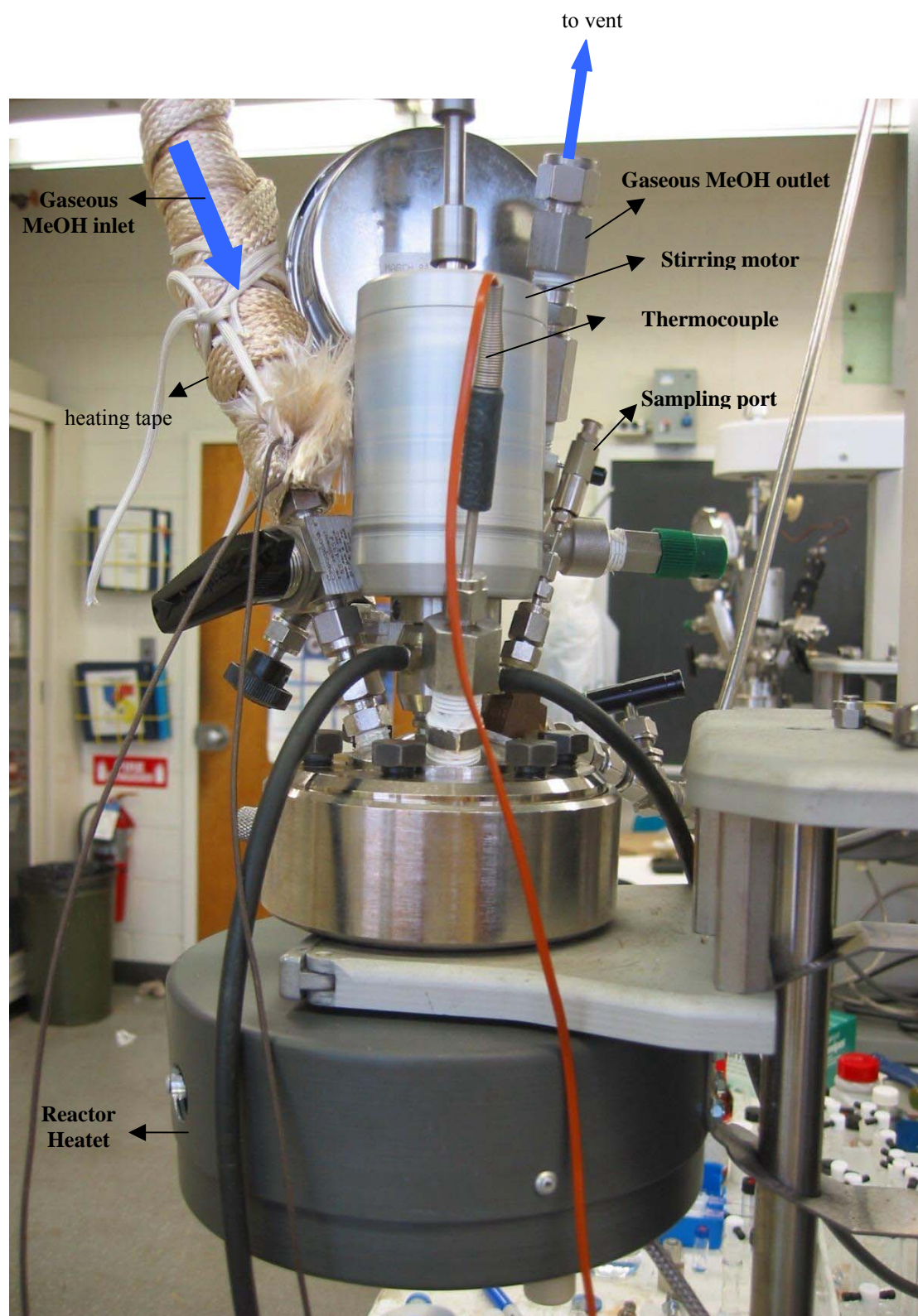


Figure 4: Picture of the Parr microreactor being currently integrated into a three phase reaction system.

A Parr batch 100 mL micro reactor has been acquired and modified to fit the specification needed for our three phase reactor. The Parr micro reactor has been already equipped with a thermocouple, stirrer, pressure manometer, glass liner and valves for material input and withdrawal. A picture of the modified reactor is shown in Figure 4. To operate the three phase system, the Parr micro reactor will initially contain the lipid feedstock (poultry fat) in contact with the catalyst (WZ). The temperature and pressure will then be taken to 120-200°C and 1-40 bar, respectively, depending on the desired reaction conditions. Afterwards, methanol will be injected as a vapor to the lipids/catalyst mixture for the reaction to start. Samples will be taken for analysis at determined time intervals to follow reaction progress. Alternatively, methanol may be injected from the beginning of the start-up period to prevent TG oligomerization. TG oligomerization may take place due to the unsaturated nature of the TG alkyl moieties.

Summary of Results

Reaction studies are underway. As anticipated, under batch reaction conditions, WZ showed low catalytic activity at 120°C probably due to methanol pore filling with site blockage to glyceride compounds. Building of a three reaction system is almost complete and three phase reaction studies using WZ will start next month (October, 2006).

Publications

Yijun Liu, Edgar Lotero and James G. Goodwin Jr. "Biodiesel synthesis using a Three Phase Reaction." To be submitted to *Green Chemistry*, November/2006 [Supported in part by this funding].

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