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# Preparation of a novel cellulose-based immobilized heteropoly acid system and its application on the biodiesel production

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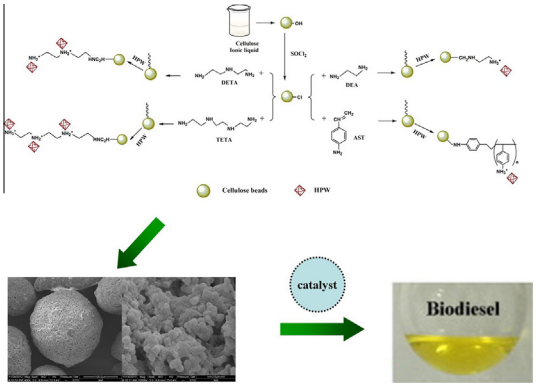
## HIGHLIGHTS

- Cellulose beads were prepared using environmental friendly ILs.
- HPWs were first immobilized on the cellulose beads with high immobilized amount.
- The cellulose-based immobilized heteropoly acid can be successfully used on the biodiesel production.
- The cellulose-based immobilized heteropoly acid can be reused more than 7 times.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Porous cellulose beads (CBs) were prepared using ionic liquid as solvent and then further modified using different reagents which were ethylenediamine (EDA), diethylenetriamine (DETA), triethylene tetramine (TETA) and 4-aminostyrene (AST). These CBs were used as carrier for immobilization of $H_3PW_{12}O_{40}$ (HPW). The immobilized catalysts were characterized by FT-IR, scanning electron microscopy, XRD, ICP atomic emission spectrophotometer. The results indicated that CB-(AST-HPW)$_n$ possessed higher amounts of HPW and stronger catalytic activity for biodiesel production. After using CB-(AST-HPW)$_n$ for yellow horn oil esterification, the conversion yield reached 96.22% under optimal conditions. The final product of biodiesel prepared with CB-(AST-HPW)$_n$ was of high quality. We conclude that cellulose-based immobilized HPW is a novel catalyst potentially suited for biodiesel production.



## 1. Introduction

Recently, the depletion of fossil fuels and increasing ecological awareness have made people to search for alternative fuels made from renewable sources [1,2]. Biodiesel is a kind of green energy because its raw material were vegetable oils and animal fats which were both renewable sources. Biodiesel is usually prepared by transesterification of triacylglycerides with methanol or ethanol, and then yield Fatty Acid Methyl Esters (FAMEs) and glycerol [3].

In the industrial production, biodiesel is produced using homogeneous alkaline such as KOH, but some problems still remain such as soap formation, glycerol recovery and the removal of inorganic substances. Moreover, homogeneous alkaline is harmful to the environment. Therefore, acid catalysts are used to circumvent these problems. But there are also some problems of acid catalysts

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such as high reaction temperature, equipment corrosion, and the removal of the acid catalyst [4].

Heteropoly acids are solid acid catalysts and have been successfully used in many reactions [5–7]. They have many advantages and can be regard as green catalysts. Heteropoly acids possess strong Brønsted acidity and the acidity of heteropoly acids are stronger than some conventional acids. Moreover, the acid sites of heteropoly acids can be more uniform and easier to control than other acid catalysts. So heteropoly acids possess higher catalytic activity in transesterification [8]. Heteropoly acids also have been successfully used for biodiesel production resulting in high yields and short reaction time [9]. However, the recovery of HPAs is difficult and complicated, because of the small particle size or the solubility in polar solvent. Recently, many porous materials have been used for the immobilization of heteropoly acids [10–12]. But heteropoly acids physically adsorbed on supports could be easily leached out because heteropoly acids have high solubility in polar solvent. Chemical bonding can be regarded as an effective method for the immobilization of HPAs, in order to reduce leaching of HPAs solvent system. Early studies showed that HPAs can be immobilized on Y-type zeolite, carbon gels, silica, mesoporous silica and so on [13–17], but most of these immobilization need high-temperature calcination, which leads to high costs. Therefore, a hotspot of research worldwide is, how to find suitable porous supports and make the HPAs immobilization system.

Cellulose is widely distributed in nature and it exhibits biocompatibility to biological molecules, easy modification with usual ligands, and suitable porosity for high adsorption capacity [18–21]. However, a major obstacle for preparation of cellulose-based supports is that cellulose cannot be dissolved in water or common organic solvents because of its well developed intermolecular hydrogen bonding [22]. Some solvents such as N-methylmorpholine N-oxide monohydrate (NMMO), LiCl/N,N-dimethylacetamide (DMAc), ammonium fluo-rides/dimethylsulfoxide which can dissolve cellulose [22,23] are all environmentally unacceptable. Very recently, it is found that some ionic liquids (ILs), called green solvents, can also dissolve cellulose. Using ILs, cellulose can be successfully prepared as several materials, such as fiber, film and beads [24–28]. Only depending on physical adsorption, HPAs cannot be immobilized on the cellulose beads effectively. Cellulose has to be modified, in order to enhance the immobilization amount and intensity. Modified cellulose beads have been used for metal adsorption [29], dye anionic adsorption [30] and drug loading [31]. Thus, modified cellulose beads can serve as alternative carriers for the immobilization of HPAs.

To the best of our acknowledgement, this is the first time that HPW is immobilized on the natural materials—cellulose. In the present investigation, we attempted to prepare a series of modified cellulose beads as solid carrier for immobilization of HPW. Cellulose-based immobilized HPW were further applied as effective catalysts for the production of biodiesel to evaluate their catalytic activities.

## 2. Experimental section

### 2.1. Materials and chemicals

$H_3PW_{12}O_{40}$ was supplied from Sigma–Aldrich. Ethylenediamine (EDA), diethylenetriamine (DETA), triethylene tetramine (TETA), 4-aminostyrene (AST), $Na_2SO_4$, Span 60, $SOCl_2$ and transformer oil were purchased from Harbin Huabo Chemical Reagent Co. Ltd (Harbin, China). ionic liquid, 1-butyl-3-methylimidazolium chloride ([C4mim]Cl) was purchased from Chengjie Chemical Reagent Co. Ltd (Shanghai, China).

### 2.2. Synthesis of cellulose-based immobilized heteropoly acid

#### 2.2.1. Preparation of cellulose beads

The cellulose solution (7 wt.%) was prepared by [C4mim]Cl. Ten gram of microcrystalline cellulose and 133 g of [C4mim]Cl were stirred for 10 h with the temperature of 90 °C. The cellulose beads were prepared using an improved method [27]. Cellulose solution (20 mL), cyclohexane (8 mL) and Tween 60 (0.8 mL) was mixed and stirred at 1500 rpm for 10 min at 90 °C (solvent I). Then, the rotational speed was reduced to 500 rpm and another solution (90 °C) which contained transformer oil (200 mL) and Span 60 (0.4 g) was poured to solvent I. Meanwhile, 100 mL of transformer oil with Span 60 (0.4 g) was stirred with $Na_2SO_4$ solution (40 mL, 0.2 mol/L) (solvent II). Then mixed solvent II with solvent I and lowered the temperature, the cellulose beads would from in the solvent.

#### 2.2.2. Synthesis of cellulose-EDA, cellulose-DETA and cellulose-TETA

Two grams of cellulose beads and 80 mL DMF were added to a 250 mL three-necked glass flask. After heating to 40 °C, 10 mL of $SOCl_2$ were then slowly added to the mixture through a constant pressure drop funnel. The mixture reacted at 90 °C under magnetic stirring for 3 h. Then, the modified cellulose beads were separated by vacuum filtration and washed in water.

Two grams of modified cellulose beads and twenty milliliter of ethanol were added to a 100 mL three-necked glass flask. At last, 25 mL EDA, DETA or TETA were quickly added into the flask. The reaction was kept at 60 °C for 12 h. The cellulose beads were filtered and thoroughly rinsed with distilled water and ethanol. The products were c dried under for 12 h and then CB-EDA, CB-TEDA, or CB-TETA were obtained.

#### 2.2.3. Synthesis of CB-$(AST)_n$

Two grams of modified cellulose beads were added to a 100 mL three-necked glass flask. Then, AST (0.8 g) dissolved in 20 mL ethanol were quickly added into the flask. The reaction systerm was kept under a $N_2$ atmosphere at 80 °C for 6 h. The cellulose beads were filtered, rinsed and dried as described in Section 2.2.1. Thereby, CB-AST was obtained.

CB-AST (2.0 g) and AST (2.0 g) were added into a glass flask with 30 mL ethanol, and the reaction was performed under $N_2$ atmosphere at 70 °C for 24 h. After that, the beads was filtered, washed with water and ethanol, and then dried under vacuum for 12 h. At last, CB-$(AST)_n$ was obtained.

#### 2.2.4. Immobilization of HPW

HPW (2.0 g) and ethanol (20 mL) was added to the flask, and the solution was slowly added to each support at appropriate quantities. The reaction was then heated at 80 °C for 12 h. The cellulose beads were filtered, washed and dried. The beads were denoted as CB-EDA-HPW, CB-DETA-HPW, CB-TETA-HPW and CB-$(AST\text{-}HPW)_n$.

### 2.3. Characterization

The surface physical properties of CB were characterized with a Micromeritics ASAP2020 (Micromeritics company, USA).

The microstructure of the cellulose beads were analyzed by scanning electron microscopy (SEM).

The XRD patterns from 3.0° to 80° were analyzed with a D/max-2400 (Rigaku, Japan) using Cu Kα radiation.

The FT-IR spectra were analyzed on a Affinity-1 spectrophotometer (Shimadzu, Japan).

The P and W contents of the catalysts were determined on an inductively coupled plasma mass spectrometry (ICP-MS) NexION 300D (PerkinElmer Company, USA).