

IONIC LIQUID CATALYST FOR PRODUCING RENEWABLE FUELS FROM WASTE OILS, PREPARATION METHOD AND APPLICATION THEREOF

TECHNICAL FIELD

[0001] The present application relates to an ionic liquid catalyst for producing renewable fuels from waste oils, a preparation method and an application thereof, and belongs to the technical field of treatment of waste oils.

BACKGROUND

[0002] With the implementation of environmental protection and carbon emission reduction initiatives, the proportion of green fuels, such as biodiesel and bio-jet fuel produced from bio-based oils and fats, has been increasing year by year, resulting in a growing shortage of raw materials. Expanding the sources of raw materials for green fuels has thus become an urgent problem. In such industries as catering, food processing, production and processing of oils and fats, meat processing, and fur processing, waste oils are generated annually, including acidified oil, waste cooking oil, swill oil, deteriorated oil and animal fat. These waste oils have the features of low utilization value and a long degradation process, and are environmental pollutants that contribute to eutrophication of water bodies and offensive odors in the air.

[0003] If these waste oils are utilized as feedstock for green fuels, favorable social benefits and considerable economic returns will be achieved. Currently, researchers have been committed to preparing renewable fuels such as diesel using the above waste oils.

[0004] However, since waste bio-based oils contain a significant number of impurities and are severely deteriorated, they contain not only natural components such as phospholipids, proteins, glycosyl diglycerides, heavy metal ions, and unsaturated substances, but also oxidative and deteriorated components including alcohols, ketones, aldehydes, and acids, as well as impurities such as dust, salts, and moisture. These substances mostly exist in the oils in the form of colloids that are difficult to separate

and remove, imparting the waste oils with corresponding thermal polymerization properties. Therefore, during the initial heating process in production, thermal polymerization occurs and the waste oils are adhered to or accumulated on a heating device, thereby leading to overheating of heat transfer device components due to blocked heat conduction, further intensifying thermal polymerization and forming a vicious cycle. If thermal polymers are not cleaned up timely, they will rapidly lead to blockage of material channels of heat exchange device components and coking on heat exchange device surfaces, making it difficult to maintain continuous production.

[0005] To address this problem, the latest method in industry involves extracting a portion of intermediate hot oil that has undergone upgrading treatment in a reactor and thus has no longer exhibited thermal polymerization properties, further heating the intermediate hot oil to a required temperature in a heating furnace, and then feeding the intermediate hot oil into a feed end where it is blended in proportion with cold initial feedstock, so that the cold feed oil is heated up and the contained impurities are also diluted. Since the process operation involves circulating flow of intermediate hot oil, in this technological method, the feed oil is heated without a heating device, thereby not only fundamentally avoiding the problem of easy coking and carbonization in the heating device, but also improving the quality of the feed oil to a certain extent, and helping to reduce the difficulties on subsequent processes.

[0006] For example, both Patent CN202211376662.X and Patent CN202310606126.2 adopt this type of method and cooperate with specific catalysts to perform hydrogenation pretreatment operations. However, the catalysts used are all carbon-based solid catalysts. Solid catalysts are prone to clogging due to the influence of impurities in the raw materials, resulting in a short overall process operation cycle. Therefore, the carbon-based catalysts used in the above two patents feature their impurity-resistant functions. However, such catalysts have high requirements for devices and are mainly used in crude oil refining. Such catalysts can be applied in industrial applications for treating waste oils, only when the feedstock oil is specially pretreated.

[0007] Aiming at the above shortcomings, researchers have begun developing liquid catalysts and ionic liquid catalysts to replace traditional carbon-based catalysts. For instance, Patent HK1212547A discloses a method for preparing biodiesel from oils using an ionic liquid catalyst, which catalyzes a transesterification reaction, and the resulting biodiesel belongs to first-generation biodiesel, different from second-generation biodiesel with a structure and performance closer to those of petroleum diesel. To produce second-generation biodiesel, Patent CN202210251260.0 discloses an oil-soluble molybdenum-based ionic liquid catalyst, which catalyzes waste oils to produce second-generation biodiesel, enabling the yield of the second-generation biodiesel in liquid-phase products to exceed 85%. To improve catalytic efficiency and reduce production costs of the catalyst, Patent CN202311642817.4 focuses on adopting a bimetallic ionic liquid catalysis method, and the yield of alkane reaches over 90%. However, the yields and other parameters obtained in the above documents are all based on studies conducted under laboratory conditions. Since waste oils contain numerous impurities and are severely deteriorated, problems such as easy coking and difficult continuous production still exist when the waste oils are used in an industrial catalytic hydrogenation process to produce products including diesel and alkanes. When such ionic liquid catalysts are used in industrial catalytic hydrogenation production, the waste oils still need to be pretreated with a treating agent or filtered to remove solid impurities. For example, Patent CN202311773339.0 specifies that waste oils need to undergo transesterification and impurity removal reactions with a pretreating agent, so as to reduce acid values and impurity contents before they are fed to produce renewable fuels such as diesel.

SUMMARY

[0008] To address the above problems, an ionic liquid catalyst for producing renewable fuels from waste oils is provided. This ionic liquid catalyst incorporates functional groups into the ionic liquid catalyst via a synthesized functional halogenated alkane monomer, thereby ensuring the lipophilicity of the ionic liquid catalyst while

removing metal ions, impurities, and phospholipids from the waste oils, achieving industrial production of second-generation biodiesel using waste oils, and further enhancing the yield of second-generation biodiesel.

[0009] In the method for producing renewable fuels from waste oils using an ionic liquid catalyst, based on heating feedstock waste oils with circulating oil, the amount of circulating oil is increased, and the concentration of impurities in the feedstock oil is significantly reduced, thereby greatly facilitating the catalysis of the liquid catalyst. In addition, a step of reheating after mixing with the liquid catalyst is eliminated, heat exchangers are omitted, and no repeated mixing of the feedstock is required, therefore, the operation process is simple, industrial promotion and application are facilitated, and the yield and quality of products are also synergistically improved.

[0010] According to one aspect of the present application, a preparation method of an ionic liquid catalyst for producing renewable fuels from waste oils is provided, including the following steps:

[0011] (1) preparation of a functional halogenated alkane monomer: a carboxyl-containing halogenated alkane is reacted with a hydroxyl-containing functional monomer, followed by treatment to obtain the functional halogenated alkane monomer, wherein the hydroxyl-containing functional monomer is selected from at least one of N-cyclohexylhydroxylamine, N-(benzyloxycarbonyl)hydroxylamine, N-hydroxymethylnicotinamide, 5-hydroxytryptamine, and N-benzylethanolamine;

[0012] (2) preparation of an intermediate B: a monomer containing tertiary amines is reacted with the functional halogenated alkane monomer, followed by treatment to obtain an intermediate A, which is then treated with a strongly basic anion exchange resin to obtain the intermediate B; and

[0013] (3) preparation of the ionic liquid catalyst: the intermediate B is mixed with polyoxometalate under heating, followed by drying to obtain the ionic liquid catalyst.

[0014] The ionic liquid catalyst prepared in the present application uses a synthesized functional halogenated alkane monomer, so that the catalyst contains long-chain alkyl groups with functional groups. The long-chain alkyl groups with functional groups are

introduced to ensure the lipophilicity of the ionic liquid catalyst and promote uniform dispersion of the ionic liquid catalyst in the feedstock oil. Moreover, during the catalytic hydrogenation process of the ionic liquid catalyst, metal ions, impurities, and phospholipids are adsorbed, so as to reduce the content of harmful substances in the feedstock oil, mitigate coking, and facilitate industrial continuous production.

[0015] Optionally, the carboxyl-containing halogenated alkane has 6 to 11 carbon atoms;

[0016] preferably, the carboxyl-containing halogenated alkane is selected from at least one of 6-chlorohexanoic acid, 7-chloroheptanoic acid, 8-chlorooctanoic acid, 9-chlorononanoic acid, 10-chlorodecanoic acid, 11-chloroundecanoic acid, 6-bromohexanoic acid, 7-bromoheptanoic acid, 8-bromooctanoic acid, 9-bromononanoic acid, 10-bromodecanoic acid, and 11-bromoundecanoic acid.

[0017] The above carboxyl-containing halogenated alkane contains at least 6 carbon atoms. The carboxyl-containing halogenated alkane is reacted with the hydroxyl-containing functional monomer to prepare a long-chain halogenated alkane monomer with functional groups. The functional halogenated alkane monomer not only retains its original long-chain alkanes but also allows the introduction of functional groups such as amino groups, cycloalkyl groups, carbonyl groups, ester groups, and a benzene ring, thereby enabling the removal of metal ions, impurities, and phospholipids.

[0018] In addition, the ionic liquid catalyst synthesized from the functional halogenated alkane prepared in the present application can further hydrogenate and convert substances such as alcohols, aldehydes, ketones, and acids in waste oils into alkanes, thereby reducing the content of impurities in the product and improving the yield of second-generation biodiesel.

[0019] Optionally, in step (3), the molar ratio of the intermediate B to the polyoxometalate is (3 to 4):1, the reaction temperature is 60 to 70°C, and the reaction time is 60 to 72 hours. Nitrogen is continuously introduced during the reaction, and a tail gas is introduced into dilute sulfuric acid. The molar ratio of dilute sulfuric acid to polyoxometalate is 1:0.06, followed by terminating the reaction when the concentration

of ammonium sulfate in the dilute sulfuric acid is no more than 1 mmol/L, drying the mixture by rotary evaporation at 80 to 90°C, and vacuum-drying at 80°C for at least 72 hours.

[0020] Optionally, the hydroxyl-containing functional monomer is selected from N-(benzyloxycarbonyl)hydroxylamine.

[0021] The N-cyclohexylhydroxylamine functional monomer contains an amino group and a cycloalkyl group, wherein the amino group can improve the removal efficiency of ions, impurities, and phospholipids, while the cycloalkyl group can enhance the lipophilicity of the ionic liquid catalyst, and realize uniform dispersion of the ionic liquid catalyst.

[0022] N-(benzyloxycarbonyl)hydroxylamine contains an amino group, an ester group, and a benzene ring, wherein the amino group and the benzene ring can remove metal ions, impurities, and phospholipids; the ester group can enhance compatibility with waste oils and realize uniform dispersion of the ionic liquid catalyst. In addition, the benzene ring structure can also improve the temperature resistance of the ionic liquid catalyst, such that the ionic liquid catalyst maintains a higher catalytic effect even at high temperatures.

[0023] N-hydroxymethylnicotinamide contains an amino group, a carbonyl group, and a pyridine ring. The carbonyl group serve to enhance lipophilicity; however, compared with ester group, its compatibility with waste oils is reduced. Therefore, the catalytic efficiency of N-hydroxymethylnicotinamide is lower than that of N-(benzyloxycarbonyl)hydroxylamine.

[0024] 5-hydroxytryptamine contains two amino groups to enhance the adsorption of metal ions, impurities, and phospholipids. However, the lipophilicity of 5-hydroxytryptamine is lower than that of N-(benzyloxycarbonyl)hydroxylamine. In addition, since the hydroxyl group is attached to the benzene ring, the reaction yield with carboxyl-containing halogenated alkane is reduced, and the production costs are increased.

[0025] N-benzylethanolamine contains a benzene ring to improve the temperature

resistance of the ionic liquid catalyst. However, compared with amino group in N-(benzyloxycarbonyl)hydroxylamine, tertiary amine group contained in N-benzylethanolamine have a reduced adsorption effect on metal ions, impurities, and phospholipids. Long-term operation may still pose a coking risk to the system.

[0026] Optionally, the tertiary amine-containing monomer is selected from at least one of trihexylamine, triheptylamine, trioctylamine, pyridine, N-methylimidazole, N-methylpyrrole, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N,N',N'-tetramethylhexamethylenediamine, and 4,4'-bipyridine.

[0027] Preferably, the tertiary amine-containing monomer is selected from at least one of N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N,N',N'-tetramethylhexamethylenediamine, and 4,4'-bipyridine.

[0028] The above tertiary amine monomer contains two tertiary amine groups. When the tertiary amine monomer is reacted with the functional halogenated alkane monomer to prepare the intermediate A, the intermediate A contains a bis-quaternary ammonium salt structure. Compared with ionic liquid catalysts prepared from other monomers, this structure exhibits higher dispersion and catalytic efficiency in waste oils. Moreover, this structure is a bisymmetric structure which ensures that the catalytic efficiency of catalytic active centers remains consistent after combining with polyoxometalate, thereby improving the uniformity of waste oil catalysis and obtaining second-generation biodiesel with higher yield and more stable performance.

[0029] Optionally, the polyoxometalate is a tri-metal polyoxometalate containing at least molybdenum and nickel metals;

[0030] preferably, the tri-metal polyoxometalate is selected from at least one of molybdenum-nickel-cobaltate, molybdenum-nickel-manganate, and molybdenum-nickel-zincate;

[0031] more preferably, the preparation method of the tri-metal polyoxometalate is as follows:

[0032] hydrogen peroxide, nickel sulfate, and a third metal sulfate are added to deionized water, and then the mixture is dropwise added to a boiling ammonium

molybdate solution, wherein the boiling state of the ammonium molybdate solution is maintained during the dropwise addition, followed by further boiling for 1-2 hours to obtain the tri-metal polyoxometalate, wherein the third metal sulfate is selected from one of cobalt sulfate, manganese sulfate, or zinc sulfate.

[0033] Although molybdenum has lower catalytic activity than nickel, the content of molybdenum involved in catalysis is high, and nickel exhibits high catalytic activity, however, a large amount of nickel cannot effectively participate in the catalytic process. Therefore, as basic catalytic metals, molybdenum and nickel in the above tri-metal polyoxometalate can synergize the catalytic properties of the two metals. When molybdenum and nickel are combined with a third metal, they can further improve the catalytic efficiency, are less susceptible to the influence of metal elements, impurities, and phospholipids in waste oils, and prolong the service life of the catalyst. In addition, the tri-metal polyoxometalate has good reaction binding efficiency with the intermediate B prepared as described above, to achieve a better catalytic hydrogenation effect on waste oil feedstock.

[0034] Optionally, the molar ratio of nickel sulfate to ammonium molybdate is (0.5 to 0.8):1; the molar ratio of cobalt sulfate, manganese sulfate, or zinc sulfate to ammonium molybdate is (0.3 to 0.4):1; hydrogen peroxide accounts for 8 to 10 wt% of ammonium molybdate.

[0035] Based on the above catalytic properties of molybdenum and nickel, the molar ratios of the trimetallic salts, namely, nickel sulfate to ammonium molybdate, and cobalt sulfate, manganese sulfate, or zinc sulfate to ammonium molybdate, correspond to the ratios of nickel, molybdenum, and the third metal (cobalt, manganese, or zinc) in the ionic liquid catalyst. Within the above ratio ranges, the catalytic activity of the ionic liquid catalyst can be enhanced, such that the ionic liquid catalyst maintains higher activity even at high temperatures required for catalytic hydrogenation. If the proportion of ammonium molybdate decreases, the overall catalytic activity of the ionic liquid catalyst will decline. If the molar ratio of nickel sulfate decreases, the service life of the ionic liquid catalyst will be shortened, thereby leading to a significant drop in

catalytic efficiency in the later stages of catalytic hydrogenation and thus reducing the product yield. If the proportion of the third metal decreases, the overall catalytic activity will be reduced and the service life of the catalyst will be shortened, thereby the product yield will be decreased.

[0036] Optionally, in step (1), the specific method of reacting the carboxyl-containing halogenated alkane with the hydroxyl-containing functional monomer and treating to obtain the functional halogenated alkane monomer is as follows:

[0037] the carboxyl-containing halogenated alkane and the hydroxyl-containing functional monomer with a molar ratio of 1:(1.1 to 1.2) are dissolved in a solvent, concentrated sulfuric acid is then added as a catalyst, and the mixture is maintained at 60 to 70°C for reaction for at least 5 hours to obtain a crude product, followed by removing the solvent by vacuum distillation, extracting the product with ethyl acetate for 3 to 5 times, and drying to obtain a target product.

[0038] Optionally, in step (2), the specific method of reacting the tertiary amine-containing monomer with the functional halogenated alkane monomer and treating to obtain the intermediate A is as follows:

[0039] the tertiary amine-containing monomer and the functional halogenated alkane monomer are dissolved in a solvent, and the mixture is heated under reflux for 22 to 24 hours, followed by removing the solvent by rotary evaporation, extracting the product for 3 to 5 times with a mixed solvent of diethyl ether and acetonitrile, and then drying to obtain the intermediate A.

[0040] Optionally, in step (2), the specific method for treating the intermediate A with a strongly basic anion exchange resin to obtain the intermediate B is as follows:

[0041] the intermediate A is dissolved in an organic solvent, and the mixture is charged into an ion exchange column packed with OH⁻-type strongly basic anion exchange resin, and is eluted with ethanol, followed by collecting a strongly basic eluate with a pH of greater than 8, and drying to obtain the intermediate B.

[0042] According to another aspect of the present application, an ionic liquid catalyst obtained by the preparation method of the ionic liquid catalyst for producing renewable

fuels from waste oils as described in any one of the above items is provided.

[0043] According to yet another aspect of the present application, a method for producing renewable fuels by treating waste oils with an ionic liquid catalyst is provided, including the following steps:

[0044] S1: circulating oil, waste oils, and the ionic liquid catalyst are mixed at a weight ratio of circulating oil: waste oils: ionic liquid catalyst of (1 to 6): 1: (0.002 to 0.005) to form a premix, the temperature of which is raised to 280 to 380°C, followed by feeding the premix into a first reactor for hydrogenation catalysis, wherein the ionic liquid catalyst is the ionic liquid catalyst obtained by the preparation method of claim 1;

[0045] S2: a gaseous effluent from the first reactor is fed into a second reactor for further hydrogenation catalysis to obtain reactants and circulating oil, and bottom effluent from the first reactor is fed into an ash-discharging hot high-pressure separator to discharge wastes containing high-ash oil and tailings;

[0046] S3: the reactants are discharged into a hot high-pressure separator to be separated into a gas phase A and a liquid phase A, wherein the gas phase A is fed into a cold high-pressure separator and is separated into circulating hydrogen, distillate oil, and residual oil; a portion of the liquid phase A is used as circulating oil, and the other portion is fed into a hot low-pressure separator and is separated into wastes containing high-ash oil and tailings as well as a liquid phase B; and

[0047] S4: the liquid phase B is fed into a fractionation tower for fractionation to obtain renewable fuels.

[0048] In some production processes, although circulating oil is returned and mixed with feedstock oil for catalytic hydrogenation, the amount of circulating oil used is relatively small. In industrial production of waste oils, due to an excessive impurity content in waste oils, coking problems still occur. After operating for a certain period of time, the system often needs to be shut down for cleaning, thereby increasing labor and material costs and reducing production efficiency. In the preparation method of the present application, circulating oil with a high circulation ratio is mixed with waste oils

for catalytic hydrogenation. Based on saving thermal energy, the colloids in the feedstock are diluted, making the production system less prone to coking, and ensuring production continuity. In the long run, industrial production capacity is still enhanced with the best comprehensive benefits. In addition, sulfides and chlorides in the feedstock are diluted or adsorbed, thereby reducing the contents of sulfur and chlorine in the product.

[0049] The first reactor used in the above method is a suspended bed reactor. During the catalytic hydrogenation process with the ionic liquid catalyst, this reactor reduces the content of impurities, thereby ensuring smooth reaction in the second reactor. In addition, in the present application, a large amount of circulating oil is used and has better affinity with the long-chain alkyl groups of the functional groups in the ionic liquid catalyst. Therefore, the circulating oil can promote uniform dispersion of the above ionic liquid catalyst in the feedstock of waste oils, enabling the ionic liquid catalyst to exert its catalytic effect more effectively, improving the catalytic efficiency and further increasing the product yield. Moreover, due to such characteristics as uniform dispersion and better affinity with circulating oil and waste oils, the long-chain alkyl groups of the functional groups in the ionic liquid catalyst in the above process can achieve a better effect in removing impurities, metal ions, and phospholipids, thereby reducing the content of impurities in the product.

[0050] Optionally, the temperature of the premix after heating is 300 to 360°C.

[0051] Optionally, the circulating oil has a density of 0.76 to 0.82 g/mL and is a biomass hydrocarbon compound with a derived cetane number (DCN) exceeding 80.

[0052] Optionally, the renewable fuels include biodiesel and/or bio-jet fuel;

[0053] preferably, the renewable fuels include hydrocarbon-based biodiesel, naphtha, and kerosene.

[0054] Optionally, the waste oils include at least one of acidified oil, waste cooking oil, swill oil, and animal fat; and the acid value of the waste oils is greater than 40 mgKOH/g.

[0055] According to yet another aspect of the present application, an application of

the method for producing renewable fuels from waste oils using any one of the above ionic liquid catalysts in the preparation of bioenergy, biodiesel, and bio-jet fuel is provided.

[0056] The beneficial effects of the present application include, but are not limited to:

[0057] 1. According to the method for producing renewable fuels by treating waste oils with the ionic liquid catalyst of the present application, the method for treating waste oils with circulating oil with a high circulation ratio and the ionic liquid catalyst is used. In combination with the efficient catalysis and impurity removal capabilities of the ionic liquid catalyst, problems of coking and clogging in devices (heating furnace pipes) caused by the feedstock are fundamentally avoided, thereby improving the operation continuity of a production system, reducing the thermal energy consumption and costs of the system, saving investment, and facilitating industrial production and processing.

[0058] 2. According to the method for producing renewable fuels by treating waste oils with the ionic liquid catalyst of the present application, the ionic liquid catalyst is improved to reduce the contents of metal ions and other impurities in waste oils, and turn the oxidized and deteriorated components into valuable resources by directly converting them into the final required products, thereby solving the technical problems of low product yield and poor product quality caused by large variety and high content of impurities in waste oils, and having significant economic benefits.

[0059] 3. According to the method for producing renewable fuels by treating waste oils with the ionic liquid catalyst of the present application, no additional treatment step is added to the original hydrogenation treatment of waste oils. Therefore, this method features a simple operation process, increases the yield of renewable fuels, achieves high production efficiency, and facilitates for industrial promotion and production.

[0060] 4. According to the ionic liquid catalyst for producing renewable fuels from waste oils of the present application, through the improvement of the long-chain alkyl groups carried by the existing ionic liquid catalyst, the lipophilicity of the ionic liquid catalyst is ensured while the metal ions, impurities, and phospholipids in waste oils are

removed. The ionic liquid catalyst can directly catalyze and treat waste oils without pretreatment to produce second-generation biodiesel, so as to reduce coking and realize industrial production.

BRIEF DESCRIPTION OF THE DRAWINGS

[0061] The accompanying drawings described herein are provided to facilitate a further understanding of the present application and form a part of the present application. The schematic embodiments of the present application and their descriptions are intended to explain the present application, and shall not constitute an improper limitation to the present application. In the accompanying drawings:

[0062] Fig. 1 is a schematic diagram of a system for producing renewable fuels from waste oils via hot oil circulation as involved in Example 1 of the present application.

[0063] Reference numerals:

[0064] 1. feedstock oil storage tank; 2. booster pump; 3. circulating oil heating furnace; 4. first reactor; 5. second reactor; 6. circulating oil pump; 7. hot high-pressure separator; 8. hot low-pressure separator; 9. distilled oil heating furnace; 10. fractionation tower; 11. first side stream oil; 12. second side stream oil; 13. third side stream oil; 14. ash-discharging hot high-pressure separator; 15. ash settling tank; 16. cold high-pressure separator; 17. circulating hydrogen compressor; 18. fresh hydrogen compressor; 19. catalyst tank.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0065] The present application is described in detail below with reference to examples, but the present application is not limited to these examples.

[0066] Unless otherwise specified, all the raw materials used in the examples of the present application are commercially available.

[0067] Unless otherwise specified, the methods adopted in the examples of the present application are conventional methods in the prior art.

[0068] Example 1

[0069] With reference to Fig.1, this example discloses a system for producing renewable fuels from waste oils via hot oil circulation. The system includes a feedstock oil storage tank 1, a booster pump 2, a circulating oil heating furnace 3, a first reactor 4, a second reactor 5, a circulating oil pump 6, a hot high-pressure separator 7, a hot low-pressure separator 8, a distilled oil heating furnace 9, a fractionation tower 10, a first side stream oil 11, a second side stream oil 12, a third side stream oil 13, an ash-discharging hot high-pressure separator 14, an ash settling tank 15, a cold high-pressure separator 16, a circulating hydrogen compressor 17, a fresh hydrogen compressor 18, and a catalyst tank 19.

[0070] The basic process for producing renewable fuels using this system is as follows:

[0071] S1: waste oils that have undergone removal of mechanical impurities and water are stored in the feedstock oil storage tank 1, dimethyl sulfide accounting for 2 wt% of the waste oils is added to the feedstock oil storage tank 1 and mixed uniformly with the waste oils, the waste oils are pressurized by the booster pump 2 and then mixed with hydrogen to form hydrogen-mixed oil; the hydrogen-mixed oil is blended with the circulating oil from the circulating heating furnace 3 and the ionic liquid catalyst from the catalyst tank 19, temperature elevation and homogenization are performed to form feed oil with a temperature of 280 to 380°C, the feed oil is fed into the first reactor 4 for catalytic hydrogenation, and reactions such as degumming and demetallization are performed, and ash impurities are removed from the reaction products;

[0072] S2: the bottom material of the first reactor 4 is discharged through the ash-discharging hot high-pressure separator 14 as wastes containing high-ash oil and tailings, the gaseous effluent from the first reactor 4 is fed into the second reactor 5 for hydrofining treatment to obtain reactants and circulating oil, the circulating oil returns to the circulating heating furnace 3 via a circulating oil pump 6 for further heating and for temperature equalization and homogenization of the hydrogen-mixed oil;

[0073] S3: the reactants flow into the hot high-pressure separator 7 for separation to obtain a gas phase A and a liquid phase A, the gas phase A is fed into the cold high-pressure separator 16 to remove moisture and water-soluble salts through separation, to

obtain circulating hydrogen, distillate oil, and residual oil, circulating hydrogen is merged with fresh hydrogen supplemented by a fresh hydrogen compressor 18, and then the pressure is boosted by the circulating hydrogen compressor 17, the mixture is introduced into a feed end to be blended with the feedstock oil for cyclic use, the combined distillate oil is fed into the fractionation tower 10 via the distilled oil heating furnace 9, and the residual oil is discharged for treatment;

[0074] a portion of liquid phase A which is used as circulating oil is fed into the circulating oil heating furnace 3 via the circulating oil pump 6; and the other portion is fed into the hot low-pressure separator 8 for separation to obtain a liquid phase B and wastes containing high-ash oil and tailings;

[0075] S4: the liquid phase B is fed into the fractionation tower 10 for fractionation, to obtain first side stream oil 11 (naphtha), second side stream oil 12 (kerosene), and third side stream oil 13 (hydrocarbon-based biodiesel), namely, various product oils that can be blended into green diesel and jet fuel, wherein the residues at the bottom of the fractionation tower 10 are mainly composed of incompletely reacted heavy oil components, and are returned to the feed end to be mixed with the feedstock oil for further treatment; and

[0076] the wastes containing high-ash oil and tailings discharged from the bottoms of the first reactor 4 and the hot low-pressure separator 8 are fed into the ash settling tank 15 for separation, the resulting residual oil is discharged for treatment, while the rest returns to an initial stage of the process and is mixed with the feedstock oil for further hydrogenation treatment.

[0077] Specifically, the first reactor operates at a temperature of 280 to 380°C, a pressure of 4 to 10 MPa, and a hydrogen-to-oil ratio of 600 to 1000; the second reactor operates at a temperature of 260 to 320°C, a pressure of 4 to 8 MPa, a liquid hourly space velocity of 0.5 to 3.0 h⁻¹, and a hydrogen-to-oil ratio of 400 to 800.

[0078] Example 2

[0079] This example relates to the preparation of an ionic liquid catalyst, and the specific steps are as follows:

[0080] (1) preparation of a functional halogenated alkane monomer: a carboxyl-containing halogenated alkane is reacted with a hydroxyl-containing functional monomer, followed by treatment to obtain the functional halogenated alkane monomer, wherein the hydroxyl-containing functional monomer is selected from at least one of N-cyclohexylhydroxylamine, N-(benzyloxycarbonyl)hydroxylamine, N-hydroxymethylnicotinamide, 5-hydroxytryptamine, and N-benzylethanolamine;

[0081] (2) preparation of an intermediate B: a tertiary amine-containing monomer is reacted with the functional halogenated alkane monomer and is treated to obtain an intermediate A, and the intermediate A is treated with a strongly basic anion exchange resin to obtain the intermediate B; and

[0082] (3) preparation of the ionic liquid catalyst: the intermediate B is mixed with polyoxometalate and heated to obtain the ionic liquid catalyst.

[0083] The carboxyl-containing halogenated alkane is selected from at least one of 6-chlorohexanoic acid, 7-chloroheptanoic acid, 8-chlorooctanoic acid, 9-chlorononanoic acid, 10-chlorodecanoic acid, 11-chloroundecanoic acid, 6-bromohexanoic acid, 7-bromoheptanoic acid, 8-bromooctanoic acid, 9-bromononanoic acid, 10-bromodecanoic acid, and 11-bromoundecanoic acid.

[0084] The tertiary amine-containing monomer is selected from at least one of trihexylamine, triheptylamine, trioctylamine, pyridine, N-methylimidazole, N-methylpyrrole, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N,N',N'-tetramethylhexamethylenediamine, and 4,4'-bipyridine.

[0085] The polyoxometalate is a tri-metal polyoxometalate containing at least molybdenum and nickel metals;

[0086] preferably, the tri-metal polyoxometalate is selected from at least one of molybdenum-nickel-cobaltate, molybdenum-nickel-manganate, and molybdenum-nickel-zincate; and the preparation method of the tri-metal polyoxometalate is as follows:

[0087] hydrogen peroxide, nickel sulfate, and a third metal sulfate are added to deionized water, and then the mixture is added dropwise to a boiling ammonium

molybdate solution, wherein the boiling state of the ammonium molybdate solution is maintained during the dropwise addition, followed by further boiling to obtain the tri-metal polyoxometalate, wherein the third metal sulfate is selected from one of cobalt sulfate, manganese sulfate, or zinc sulfate.

[0088] Ionic liquid catalysts 1# to 13# and comparative ionic liquid catalysts D1# to D2# are prepared according to the above preparation method, and the specific preparation methods are as follows:

[0089] Ionic liquid catalyst 1#

[0090] (1) Preparation of a functional halogenated alkane monomer: 0.1 mol of 6-chlorohexanoic acid and 0.11 mol of N-cyclohexylhydroxylamine are dissolved in a mixed solvent of ethanol and N,N-dimethylformamide (DMF) with the ratio of ethanol to DMF of 1:1 by volume, and concentrated sulfuric acid accounting for 2 wt% of 6-chlorohexanoic acid is added as a catalyst, followed by maintaining the mixture at 60°C for 8 hours for reaction to obtain a crude product, removing the solvent by vacuum distillation, extracting the product with ethyl acetate for three times, and drying to obtain the target product;

[0091] (2) preparation of intermediate B: 0.08 mol of trihexylamine and 0.08 mol of functional halogenated alkane monomer are dissolved in a mixed solvent of ethanol and acetone with the ratio of ethanol to acetone of 1:1 by volume, and the mixture is heated under reflux for 24 hours, followed by removing the solvent by rotary evaporation, extracting the product for three times with a mixed solvent of diethyl ether and acetonitrile at a ratio 1:1 by volume, and then drying to obtain an intermediate A; the intermediate A is dissolved in ethanol, and the mixture is charged into an ion exchange column packed with OH⁻-type strongly basic anion exchange resin and is eluted with ethanol, followed by collecting a strongly basic eluate with a pH of greater than 8, and drying at 80°C for 24 hours to obtain the intermediate B;

[0092] (3) preparation of ionic liquid catalyst: hydrogen peroxide accounting for 8 wt% of ammonium molybdate, 0.05 mol of nickel sulfate, and 0.04 mol of zinc sulfate are added to deionized water, and then the mixture is dropwise added to a boiling solution

of 0.1 mol of ammonium molybdate at a dropping rate of 2 drops per second, wherein the boiling state of the ammonium molybdate solution is maintained during the dropwise addition, followed by further boiling for 1 hour to obtain the tri-metal polyoxometalate; the intermediate B and the tri-metal polyoxometalate are mixed at a molar ratio of 3:1, and the mixture is heated to 60°C and maintained at 60°C for 72 hours, wherein nitrogen is continuously introduced during the reaction, and a tail gas is fed into the dilute sulfuric acid with the molar ratio of dilute sulfuric acid to tri-metal polyoxometalate of 1:0.06, followed by terminating the reaction when the concentration of ammonium sulfate in the dilute sulfuric acid is no more than 1 mmol/L, drying the mixture by rotary evaporation at 80°C for 6 hours, and vacuum-drying at 80°C for 72 hours to obtain the ionic liquid catalyst 1#.

[0093] Ionic liquid catalyst 2#

[0094] (1) Preparation of a functional halogenated alkane monomer: 0.1 mol of 11-chloroundecanoic acid and 0.11 mol of N-hydroxymethylnicotinamide are dissolved in a mixed solvent of ethanol and DMF with the ratio of ethanol to DMF of 1:1 by volume, and concentrated sulfuric acid accounting for 2 wt% of 11-chloroundecanoic acid is added as a catalyst, followed by maintaining the mixture at 70°C for 5 hours for reaction to obtain a crude product, removing the solvent by vacuum distillation, extracting the product with ethyl acetate for five times, and drying to obtain the target product;

[0095] (2) preparation of intermediate B: 0.08 mol of pyridine and 0.08 mol of functional halogenated alkane monomer are dissolved in a mixed solvent of ethanol and acetone with the ratio of ethanol to acetone of 1:1 by volume, and the mixture is heated under reflux for 22 hours, followed by removing the solvent by rotary evaporation, extracting the product for five times with a mixed solvent of diethyl ether and acetonitrile at a ratio of 1:1 by volume, and then drying to obtain an intermediate A; the intermediate A is dissolved in ethanol, and the mixture is charged into an ion exchange column packed with OH⁻-type strongly basic anion exchange resin and is eluted with ethanol, followed by collecting a strongly basic eluate with a pH of greater than 8, and drying at 80°C for 24 hours to obtain the intermediate B;

[0096] (3) preparation of ionic liquid catalyst: hydrogen peroxide accounting for 10 wt% of ammonium molybdate, 0.08 mol of nickel sulfate, and 0.03 mol of manganese sulfate are added to deionized water, and then the mixture is dropwise added to a boiling solution of 0.1 mol of ammonium molybdate at a dropping rate of 1 drop per second, wherein the boiling state of the ammonium molybdate solution is maintained during the dropwise addition, followed by further boiling for 2 hours to obtain the tri-metal polyoxometalate; the intermediate B and the tri-metal polyoxometalate is mixed at a molar ratio of 4:1, and the mixture is heated to 70°C, and maintained at 70°C for 60 hours, wherein nitrogen is continuously introduced during the reaction, and a tail gas is fed into the dilute sulfuric acid with the molar ratio of dilute sulfuric acid to the tri-metal polyoxometalate of 1:0.06, followed by terminating the reaction when the concentration of ammonium sulfate in the dilute sulfuric acid is no more than 1 mmol/L, drying the mixture by rotary evaporation at 90°C for 4 hours, and vacuum-drying at 80°C for 72 hours to obtain the ionic liquid catalyst 2#.

[0097] Ionic liquid catalyst 3#

[0098] (1) Preparation of a functional halogenated alkane monomer: 0.1 mol of 9-bromononanoic acid and 0.11 mol of N-(benzyloxycarbonyl)hydroxylamine are dissolved in a mixed solvent of methanol and dimethyl sulfoxide with the ratio of methanol to dimethyl sulfoxide of 1:1 by volume, and concentrated sulfuric acid accounting for 2 wt% of 9-bromononanoic acid is added as a catalyst, followed by maintaining the mixture at 65°C for 6 hours for reaction to obtain a crude product, removing the solvent by vacuum distillation, extracting the product with ethyl acetate for five times, and drying to obtain the target product;

[0099] (2) preparation of intermediate B: 0.08 mol of N-methylimidazole and 0.08 mol of functional halogenated alkane monomer are dissolved in a mixed solvent of methanol and chloroform with the ratio of methanol to chloroform of 1:1 by volume, and the mixture is heated under reflux for 22 hours, followed by removing the solvent by rotary evaporation, extracting the product for five times with a mixed solvent of diethyl ether and acetonitrile at a ratio of 1:1 by volume, and then drying to obtain an

intermediate A; the intermediate A is dissolved in methanol, and the mixture is charged into an ion exchange column packed with OH⁻-type strongly basic anion exchange resin and is eluted with methanol, followed by collecting a strongly basic eluate with a pH of greater than 8, and drying at 80°C for 24 hours to obtain the intermediate B;

[0100] (3) preparation of ionic liquid catalyst: hydrogen peroxide accounting for 10 wt% of ammonium molybdate, 0.06 mol of nickel sulfate, and 0.04 mol of cobalt sulfate are added to deionized water, and then the mixture is dropwise added to a boiling solution of 0.1 mol of ammonium molybdate at a dropping rate of 2 drops per second, wherein the boiling state of the ammonium molybdate solution is maintained during the dropwise addition, followed by further boiling for 1.5 hours to obtain the tri-metal polyoxometalate; the intermediate B and the tri-metal polyoxometalate are mixed at a molar ratio of 4:1, and the mixture is heated to 65°C, and maintained at 65°C for 70 hours, wherein nitrogen is continuously introduced during the reaction, and a tail gas is fed into the dilute sulfuric acid with the molar ratio of dilute sulfuric acid to the tri-metal polyoxometalate of 1:0.06, followed by terminating the reaction when the concentration of ammonium sulfate in the dilute sulfuric acid is no more than 1 mmol/L, drying the mixture by rotary evaporation at 80°C for 6 hours, and vacuum-drying at 80°C for 72 hours to obtain the ionic liquid catalyst 3#.

[0101] Ionic liquid catalyst 4#

[0102] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that 5-hydroxytryptamine is used to replace N-(benzyloxycarbonyl) hydroxylamine, and the rest is the same as that of ionic liquid catalyst 3#.

[0103] Ionic liquid catalyst 5#

[0104] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that N-benzylethanolamine is used to replace N-(benzyloxycarbonyl) hydroxylamine, and the rest is the same as that of ionic liquid catalyst 3#.

[0105] Ionic liquid catalyst 6#

[0106] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that N-methylpyrrole is used to replace N-methylimidazole, and the rest is the same as that of

ionic liquid catalyst 3#.

[0107] Ionic liquid catalyst 7#

[0108] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that 0.04 mol of N,N,N',N'-tetramethylethylenediamine is used to replace 0.08 mol of N-methylimidazole, and the rest is the same as that of ionic liquid catalyst 3#.

[0109] Ionic liquid catalyst 8#

[0110] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that 0.04 mol of N,N,N',N'-tetramethyl-1,4-butanediamine is used to replace 0.08 mol of N-methylimidazole, ethanol is used to replace methanol as the solvent, and the rest is the same as that of ionic liquid catalyst 3#.

[0111] Ionic liquid catalyst 9#

[0112] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that 0.04 mol of N,N,N',N'-tetramethylhexanediamine is used to replace 0.08 mol of N-methylimidazole, acetone is used to replace chloroform as the solvent, and the rest is the same as that of ionic liquid catalyst 3#.

[0113] Ionic liquid catalyst 10#

[0114] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that 0.04 mol of 4,4'-bipyridine is used to replace 0.08 mol of N-methylimidazole, and the rest is the same as that of ionic liquid catalyst 3#.

[0115] Ionic liquid catalyst 11#

[0116] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that, in step (3), cobalt sulfate is replaced by 0.1 mol of nickel sulfate; the rest is the same as that of ionic liquid catalyst 3#.

[0117] Ionic liquid catalyst 12#

[0118] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that, in step (3), nickel sulfate is replaced by 0.1 mol of cobalt sulfate, and the rest is the same as that of ionic liquid catalyst 3#.

[0119] Ionic liquid catalyst 13#

[0120] This ionic liquid catalyst differs from ionic liquid catalyst 3# in that, in step

(3), nickel sulfate is replaced by manganese sulfate, and the rest is the same as that of ionic liquid catalyst 3#.

[0121] Comparative ionic liquid catalyst D1#

[0122] This comparative ionic liquid catalyst differs from ionic liquid catalyst 3# in that 1-bromododecane is used to replace the functional halogenated alkane monomer synthesized in step (1), and the rest is the same as that of ionic liquid catalyst 3#.

[0123] Comparative ionic liquid catalyst D2#

[0124] This comparative ionic liquid catalyst differs from ionic liquid catalyst 3# in that, in step (3), a single-metal salt is used to replace a tri-metal polyoxometalate, and further a single-metal ionic liquid catalyst is synthesized. The specific steps of step (3) are as follows: hydrogen peroxide in an amount equal to that used in ionic liquid catalyst 3# is added to deionized water, and then the mixture is dropwise added to a boiling solution of 0.1 mol of ammonium molybdate at a dropping rate of 2 drops per second, wherein the boiling state of the ammonium molybdate solution is maintained during the dropwise addition, followed by further boiling for 1.5 hours to obtain molybdenum metal salt; the intermediate B and molybdenum metal salt are mixed at a molar ratio of 4:1, and the mixture is heated to 65°C, and maintained at 65°C for 70 hours, wherein nitrogen is continuously introduced during the reaction, and a tail gas is fed into the dilute sulfuric acid with the molar ratio of dilute sulfuric acid to molybdic acid of 1:0.06, followed by terminating the reaction when the concentration is no more than 1 mmol/L, drying the mixture by rotary evaporation at 80°C for 6 hours, and vacuum-drying at 80°C for 72 hours to obtain the comparative ionic liquid catalyst D2#. The rest is the same as that of ionic liquid catalyst 3#.

[0125] Example 3

[0126] A method for obtaining renewable fuels by hydrotreating waste oils using the system for producing renewable fuels from waste oils via hot oil circulation in Example 1 is adopted, wherein the ionic liquid catalyst used in this example is the ionic liquid catalyst prepared in Example 2. The differences in the specific treatment methods are shown in Table 1, where “-” in Table 1 indicates consistency with Method 4. The

circulating oil used with a density of 0.76 to 0.82 g/mL is a biomass hydrocarbon compound with a DCN exceeding 80.

[0127]

Table 1

Exa mpl es	Weight ratio of circulati ng oil, waste oils and ionic liquid catalyst	Typ es of wast e oils	Ioni c liqu id cata lyst s	First reactor			Second reactor			
				Temp eratur e (°C)	Pre ssur e (M Pa)	Hydro gen to oil ratio	Temp eratur e (°C)	Pres sure (MP a)	liquid hourly space velocit y (h ⁻¹)	Hydr ogen to oil ratio
Met hod 1	4:1:0.00 4	Acid ified oil	3#	300	5	800	280	4	1.0	400
Met hod 2	6:1:0.00 2	Swil l oil	1#	280	4	600	260	4	0.5	400
Met hod 3	1:1:0.00 5	Ani mal fat	2#	380	10	1000	320	8	3.0	800
Met hod 4	4:1:0.00 4	Was te coo king oil	3#	320	8	800	300	6	2.0	600
Met hod 5	-	-	4#	-	-	-	-	-	-	-
Met hod 6	-	-	5#	-	-	-	-	-	-	-

Met hod 7	-	-	6#	-	-	-	-	-	-	-
Met hod 8	-	-	7#	-	-	-	-	-	-	-
Met hod 9	-	-	8#	-	-	-	-	-	-	-
Met hod 10	-	-	9#	-	-	-	-	-	-	-
Met hod 11	-	-	10#	-	-	-	-	-	-	-
Met hod 12	-	-	11#	-	-	-	-	-	-	-
Met hod 13			12#							
Met hod 14			13#							
Met hod 15	-	-	D1 #	-	-	-	-	-	-	-
Met hod 16	-	-	D2 #	-	-	-	-	-	-	-
Met hod	0.5:1:0.0 04	-	-	-	-	-	-	-	-	-

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[0128] Test example

[0129] The hydrocarbon-based biodiesel, naphtha, and kerosene prepared by each method in Example 3 are calculated, and tested. The test results are shown in the following Tables 2 to 4.

[0130] Table 2 Hydrocarbon-based biodiesel

Example s	Yield (%)	Contents of C15 to C18 alkanes (%)	Sulphur content (mg/kg)	Total contamination content (mg/kg)	Acidity (mg/100 mL)	Oxidation stability (mg/100m L)
Method 1	60.3	74.5	3	15	3.4	1.5
Method 2	59.3	73.4	4	17	3.9	1.7
Method 3	60.0	73.5	4	16	3.8	1.7
Method 4	60.2	74.6	3	15	3.5	1.5
Method 5	59.2	72.2	5	19	4.8	2.4
Method 6	58.4	72.5	5	18	4.7	2.3
Method 7	60.3	74.1	3	16	3.7	1.6
Method 8	60.8	74.7	3	14	3.1	1.2
Method 9	61.1	75.0	2	13	2.3	0.9
Method 10	61.2	75.2	1	12	1.2	0.8
Method	60.8	74.9	2	13	2.5	1.1

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Method 12	59.0	72.8	5	18	4.6	1.9
Method 13	58.8	72.7	5	18	4.6	2.0
Method 14	58.6	72.5	5	19	4.7	2.0
Method 15	59.1	70.3	7	28	8.4	4.5
Method 16	59.3	71.5	7	27	7.1	3.8
Method 17	58.8	71.9	6	20	5.9	2.5

[0131] In Table 2, the contents of C15 to C18 alkanes are tested and calculated in accordance with SH/T 0410, and the index is considered qualified if it is no less than 70%; the sulfur content is tested and calculated in accordance with GB/T 34100, and the index is considered qualified if it is no more than 10 mg/kg; the total contamination content refers to the total content of all contaminations including metal ions, impurities and phospholipids, and are tested and calculated in accordance with GB/T 33400, and the index is considered qualified if it is no more than 24 mg/kg; the acidity, expressed as KOH, is tested and calculated in accordance with GB/T 7304, and the index is considered qualified if it is no more than 5 mg/100 mL; the oxidation stability, expressed as total insoluble matter, is tested and calculated in accordance with SH/T 0175, and the index is considered qualified if it is no more than to 2.5 mg/100 mL.

[0132] Table 3 Naphtha

Examples	Yield (%)	Sulfur content (mg/kg)	Iron content (g/L)	Solvent-unwashed gum content (mg/100mL)	Phosphorus content (g/L)
Method 1	0.5	2	0.004	21.5	-
Method 2	0.7	3	0.006	22.5	0.0001
Method 3	0.6	3	0.005	22.4	0.0001

Method 4	0.5	2	0.004	22.0	-
Method 5	0.9	4	0.008	25.3	0.0002
Method 6	0.9	3	0.008	25.1	0.0001
Method 7	0.5	2	0.005	22.3	-
Method 8	0.4	2	0.004	21.8	-
Method 9	0.3	1	0.002	19.2	-
Method 10	0.3	1	0.002	19.0	-
Method 11	0.4	1	0.003	20.6	-
Method 12	0.8	3	0.007	23.7	0.0001
Method 13	0.8	3	0.007	23.9	0.0001
Method 14	0.9	3	0.007	24.5	0.0001
Method 15	1.7	5	0.013	29.7	0.0007
Method 16	1.4	5	0.010	29.5	0.0009
Method 17	1.2	4	0.009	38.9	0.0006

[0133] In Table 3, the sulfur content is tested and calculated in accordance with SH/T 0689, and the index is considered qualified if it is no more than 10 mg/kg; the iron content is tested and calculated in accordance with SH/T 0712, and the index is considered qualified if it is no more than 0.01 g/L; the gum content is tested and calculated in accordance with GB/T 8019, and the unwashed solvent gum content is considered qualified if it is no more than 30 mg/100 mL; the phosphorus content is tested and calculated in accordance with SH/T 0020, and the index is considered qualified if it is no more than 0.0002. The “-” in Table 3 indicates that the corresponding component was not detected.

[0134]

Table 4 Kerosene

Examples	Yield (%)	Halogen content (mg/kg)	Metal content (mg/kg)	Sulfur content (mg/kg)	Acid value (mgKOH/g)
Method 1	26.3	0.3	1.4	5	0.003
Method 2	26.2	0.5	1.6	7	0.006
Method 3	25.7	0.4	1.6	7	0.005
Method 4	26.2	0.3	1.5	5	0.003
Method 5	23.8	0.6	1.9	10	0.009
Method 6	24.9	0.6	1.8	9	0.009
Method 7	25.5	0.4	1.5	6	0.004
Method 8	26.1	0.3	1.4	5	0.003
Method 9	26.3	0.2	1.2	3	0.001
Method 10	26.3	0.1	1.2	3	0.001
Method 11	26.2	0.2	1.3	4	0.002
Method 12	24.6	0.5	1.7	9	0.007
Method 13	24.7	0.6	1.7	9	0.008
Method 14	24.7	0.6	1.8	9	0.008
Method 15	22.2	0.8	2.5	15	0.013
Method 16	22.5	0.7	2.4	13	0.012
Method 17	23.6	0.7	2.2	12	0.010

[0135] In Table 4, the halogen content is tested and calculated in accordance with ASTM D7359, and the index is considered qualified if it is no more than 1 mg/kg; the metal content refers to a total content of aluminum, calcium, cobalt, chromium, copper, iron, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, phosphorus, lead, palladium, platinum, tin, strontium, titanium, vanadium, and zinc. The metal content is tested and calculated in accordance with NB/SH/T 0892, and the content of each metal is considered qualified if it is no more than 0.1 mg/kg. There are 22 metal elements listed above; therefore, the total metal content in Table 4 is considered qualified if it is no more than 2.2 mg/kg. The sulfur content is tested and calculated in accordance with SH/T 2689, and the index is considered qualified if it is

no more than 15 mg/kg; and the acid value is tested and calculated in accordance with GB/T 12574, and the index is considered qualified if it is no more than 0.015 mgKOH/g.

[0136] Based on the above data, it can be known that the ionic liquid catalyst prepared in the present application is able to catalyze the catalytic hydrogenation of waste oils to produce naphtha, kerosene, and hydrocarbon-based biodiesel. The total yields of the three products for each method are as follows: Method 1: 87.1%, Method 2: 86.2%, Method 3: 86.3%, Method 4: 86.9%, Method 5: 83.9%, Method 6: 84.2%, Method 7: 86.3%, Method 8: 87.3%, Method 9: 87.7%, Method 10: 87.8%, Method 11: 87.4%, Method 12: 84.4%, Method 13: 84.3%, Method 14: 84.2%, Method 15: 83.0%, Method 16: 83.2%, and Method 17: 83.6%. This proves that the use of the ionic liquid catalyst in the present application for catalyzing waste oils can generate significant economic benefits. Meanwhile, all the above methods can be carried out for mass production in the system described in Example 1, without causing coking to devices, and with no need of adding ionic liquid catalysts to the waste oils for additional pretreatment, thereby reducing the cost of recycling and reuse of waste oils, and improving the operational convenience and controllability of the process.

[0137] From the comparison between Method 4 and Methods 5 and 6, it can be known that the type of hydroxyl-containing functional monomer can change the type of functional groups in the long chains carried by the ionic liquid catalyst, thereby affecting the catalytic efficiency of the ionic liquid catalyst and the removal effect on metal ions, impurities, and phospholipids.

[0138] From the comparison between Methods 7 to 11 and Method 4, it can be known that the type of tertiary amine monomer in the ionic liquid catalyst also affects the catalytic efficiency and the removal effect on metal ions, impurities, and phospholipids. The tertiary amine monomers used in Methods 8 to 11 all contain two tertiary amines, to form two quaternary ammonium salt groups. Compared with tertiary amine monomers containing only one tertiary amine, the catalytic activity is higher and the removal effect on metal ions, impurities, and phospholipids is better.

[0139] From the comparison between Method 12, method 13 and Method 4, it can be

known that under the condition that the intermediate B remains unchanged, compared with molybdenum-nickel-cobalt tri-metal polyoxometalate, the bimetallic salts of molybdenum-cobalt catalyst and molybdenum-nickel catalyst alone will reduce the catalytic efficiency of the ionic liquid catalysts and weaken the removal effect on metal ions, impurities, and phospholipids under the same catalytic conditions. Therefore, in the present application, the tri-metal polyoxometalate which takes molybdenum and nickel as the basis and which is supplemented with a third metal exhibits a better coordination effect with the intermediate B. From the comparison between Method 14 and Method 4, it is known that when the molybdenum-nickel base metals are replaced by molybdenum-manganese base metals, the catalytic activity and the removal effect on metal ions, impurities, and phospholipids are both reduced, even under the condition of the same content and coordination with the third catalytic metal. This proves that the tri-metal polyoxometalate in the present application makes full use of the catalytic properties of molybdenum and nickel to achieve an optimal catalytic effect. From the comparison between Method 16 and Method 4, it can be known that the catalytic efficiency of the ionic liquid catalyst D2# (formed by a single metal and intermediate B) decreases more significantly, and the removal effect on metal ions, impurities, and phospholipids also decreases more greatly compared with that of the bimetallic salts used in Method 12.

[0140] From the comparison between Method 15 and Method 4, it can be known that, compared with the ionic liquid catalyst prepared from common long-chain alkyl halides, the ionic liquid catalyst prepared in the present application using the synthesized functional halogenated alkane monomer can significantly improve both the catalytic efficiency for waste oils and the removal effect on metal ions, impurities, and phospholipids, making it more suitable for the industrial catalysis of waste oils to produce renewable fuels such as second-generation biodiesel. In addition, as the process proceeds, the coking rate in Method 15 is significantly higher than that in Method 4. When the comparative ionic liquid catalyst D1# is used for hydrogenation catalysis of waste oils to produce second-generation biodiesel, the system needs to be shut down

after operating for a certain period, and coking areas need to be cleaned before normal operation, therefore, the production efficiency is significantly reduced compared with that in Method 4.

[0141] From the comparison between Method 17 and Method 4, it can be known that a decrease in the proportion of circulating oil leads to a reduction in the dilution effect on the feedstock waste oils, thereby lowering the dispersion effect of the ionic liquid catalyst in the waste oils, and further reducing both the catalytic efficiency and the removal effect on metal ions, impurities, and phospholipids. In addition, Method 17 is the same as Method 15, as the process proceeds, the coking rate of Method 17 is significantly higher than that in Method 4. The system needs to be shut down after operating for a certain period of time to clean the coking areas, resulting in batch production, and the production efficiency of Method 17 is also significantly lower than that of Method 4.

[0142] The foregoing are merely examples of the present application, and the protection scope of the present application is not limited by these specific examples, but shall be determined by the claims of the present application. For those skilled in the art, various modifications and changes may be made to the present application. Any modification, equivalent substitution, improvement and the like made within the technical concept and principles of the present application shall be included in the protection scope of the present application.

CLAIMS

1. A preparation method of an ionic liquid catalyst for producing renewable fuels from waste oils, comprising the following steps:

(1) preparation of a functional halogenated alkane monomer: reacting a carboxyl-containing halogenated alkane with a hydroxyl-containing functional monomer, followed by treatment to obtain the functional halogenated alkane monomer, wherein the hydroxyl-containing functional monomer is selected from at least one of N-cyclohexylhydroxylamine, N-(benzyloxycarbonyl)hydroxylamine, N-hydroxymethylnicotinamide, 5-hydroxytryptamine, and N-benzylethanolamine;

(2) preparation of an intermediate B: reacting a tertiary amine-containing monomer with the functional halogenated alkane monomer and treating to obtain an intermediate A, which is then treated with a strongly basic anion exchange resin to obtain the intermediate B; and

(3) preparation of the ionic liquid catalyst: mixing the intermediate B with polyoxometalate and reacting under heating, followed by drying to obtain the ionic liquid catalyst.

2. The preparation method of the ionic liquid catalyst for producing renewable fuels from waste oils of claim 1, wherein the carboxyl-containing halogenated alkane has 6 to 11 carbon atoms;

preferably, the carboxyl-containing halogenated alkane is selected from at least one of 6-chlorohexanoic acid, 7-chloroheptanoic acid, 8-chlorooctanoic acid, 9-chlorononanoic acid, 10-chlorodecanoic acid, 11-chloroundecanoic acid, 6-bromohexanoic acid, 7-bromoheptanoic acid, 8-bromooctanoic acid, 9-bromononanoic acid, 10-bromodecanoic acid, and 11-bromoundecanoic acid.

3. The preparation method of the ionic liquid catalyst for producing renewable fuels from waste oils of claim 1, wherein the hydroxyl-containing functional monomer is selected from N-(benzyloxycarbonyl)hydroxylamine.

4. The preparation method of the ionic liquid catalyst for producing renewable fuels from waste oils of claim 1, wherein the tertiary amine-containing monomer is

selected from at least one of trihexylamine, triheptylamine, trioctylamine, pyridine, N-methylimidazole, N-methylpyrrole, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N,N',N'-tetramethylhexamethylenediamine, and 4,4'-bipyridine.

5. The preparation method of the ionic liquid catalyst for producing renewable fuels from waste oils of claim 1, wherein the polyoxometalate is a tri-metal polyoxometalate containing at least molybdenum and nickel metals;

preferably, the tri-metal polyoxometalate is selected from at least one of molybdenum-nickel-cobaltate, molybdenum-nickel-manganate, and molybdenum-nickel-zincate;

more preferably, the preparation method of the tri-metal polyoxometalate is as follows:

adding hydrogen peroxide, nickel sulfate, and a third metal sulfate to deionized water, and then adding the mixture dropwise to a boiling ammonium molybdate solution, wherein the boiling state of the ammonium molybdate solution is maintained during the dropwise addition, followed by further boiling for 1 to 2 hours to obtain the tri-metal polyoxometalate, wherein the third metal sulfate is selected from one of cobalt sulfate, manganese sulfate, or zinc sulfate.

6. An ionic liquid catalyst obtained by the preparation method of the ionic liquid catalyst for producing renewable fuels from waste oils of any one of claims 1 to 5.

7. A method for producing renewable fuels by treating waste oils with an ionic liquid catalyst, comprising the following steps:

S1: mixing circulating oil, waste oils, and the ionic liquid catalyst at a weight ratio of circulating oil: waste oils: ionic liquid catalyst of (1 to 6): 1: (0.002 to 0.005) to form a premix, raising the temperature of the premix to 280 to 380°C, followed by feeding the premix into a first reactor (4) for hydrogenation catalysis, wherein the ionic liquid catalyst is the ionic liquid catalyst obtained by the preparation method of claim 1;

S2: feeding a gaseous effluent from the first reactor (4) into a second reactor (5) for further hydrogenation catalysis to obtain reactants and circulating oil, and feeding

bottom effluent from the first reactor (4) into an ash-discharging hot high-pressure separator (14) to discharge wastes containing high-ash oil and tailings;

S3: discharging the reactants into a hot high-pressure separator (7) to be separated into a gas phase A and a liquid phase A, wherein the gas phase A is fed into a cold high-pressure separator (16) and is separated into circulating hydrogen, distillate oil, and residual oil; a part of the liquid phase A is used as circulating oil, and the other part is fed into a hot low-pressure separator (8) and is separated into wastes containing high-ash oil and tailings as well as a liquid phase B; and

S4: feeding the liquid phase B into a fractionation tower (10) for fractionation to obtain renewable fuels.

8. The method for producing renewable fuels by treating waste oils with the ionic liquid catalyst of claim 7, wherein the temperature of the premix after heating is 300 to 360°C;

the waste oils comprise at least one of acidified oil, waste cooking oil, swill oil, and animal fat;

the acid value of the waste oils is greater than 40 mgKOH/g;

the renewable fuels include biodiesel and/or bio-jet fuel; and

preferably, the renewable fuels include hydrocarbon-based biodiesel, naphtha, and kerosene.

9. The method for producing renewable fuels by treating waste oils with the ionic liquid catalyst of claim 7, wherein the circulating oil has a density of 0.76 to 0.82 mL/g and is a biomass hydrocarbon compound with a derived cetane number (DCN) exceeding 80.

10. The application of the method for producing renewable fuels by treating waste oils with the ionic liquid catalyst of any one of claims 7 to 9 in the preparation of bioenergy, biodiesel and bio-jet fuel.