

**MILD CATALYTIC METHOD TO SELECTIVELY PRODUCE AVIATION FUEL
FROM PLASTIC WASTE**

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore application No. 10202301879R filed on 30 June 2023, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] The present disclosure generally relates to a catalytic method of producing aviation fuel from plastic waste. In particular, the present disclosure relates to a catalytic method of producing sustainable aviation fuel from plastic waste under mild conditions, in the presence of a catalyst.

BACKGROUND

[0003] The widespread applications of plastics in automotive, packaging, building, construction and single-use protective equipment such as masks have led to a rapid increase in plastic usage and the generation of plastic waste. However, plastic waste cannot be easily broken down by microorganisms and must be destroyed by incineration, a process that emits greenhouse gases, including carbon dioxide, contributing to global warming. This issue is particularly pressing for small countries like Singapore, which have limited land for landfills. Addressing the problem of plastic waste is crucial for reducing environmental harm and one possible way is to transform it into valuable products that are required by the society, such as sustainable aviation fuel (SAF).

[0004] Currently, aviation fuel is mainly produced from crude oil and natural gas, with the extraction, refinement, and transportation processes associated with these fossil fuels emitting substantial amounts of carbon dioxide. By contrast, sustainable aviation fuel produced from

plastic waste can reduce the demand for crude oil and natural gas, consequently reducing carbon dioxide emissions throughout the aviation fuel production cycle. While the consumption of SAF does generate carbon dioxide, the circular upcycling of plastic waste into SAF through an economically and energy-efficient process represents a more sustainable interim solution. However, the current method of converting plastic waste into aviation fuel typically involves high-temperature processes such as pyrolysis or gasification.

[0005] Pyrolysis is a process where organic materials, including plastic waste, are heated in the absence of oxygen to temperature typically ranging from 500°C to 800°C. Gasification is another high-temperature process that involves reacting carbonaceous feedstocks, such as plastic waste, with a controlled amount of oxygen and/or steam at temperatures typically exceeding 700°C. Although both processes offer possibilities to convert plastic waste into aviation fuel, these processes require an additional hydrodeoxygenation/ hydrogenation step to upgrade unsaturated oil to saturated products for the use in aviation fuel. In addition, careful control of operating conditions, such as temperature, pressure, and residence time, to optimize product yields and quality while minimizing emissions and the huge energy consumption due to harsh temperatures required have to be considered.

[0006] It is therefore desirable to provide a method of producing sustainable aviation fuel from plastic waste which seeks to address at least one of the problems described hereinabove, or at least to provide an alternative.

SUMMARY

[0007] In accordance with a first aspect of the present disclosure, a catalytic method of producing sustainable aviation fuel from plastic waste is provided. The method comprises subjecting plastic waste to hydrocracking under mild conditions in the presence of a catalyst to obtain a sustainable aviation fuel, wherein the mild conditions include heating the plastic waste at a temperature of less than 300°C, under 2×10^6 Pa of hydrogen pressure, and within 3 hours;

and wherein the catalyst is a bimetallic Rh-based catalyst, Rh_2MoO_x , supported on an Al-SBA-15 material, represented by $\text{Rh}_2\text{MoO}_x/\text{Al-SBA-15}$.

[0008] In some embodiments, the sustainable aviation fuel comprises hydrocarbons with carbon ranging from C_6 - C_{16} .

[0009] In some embodiments, the hydrocracking is performed in the absence of a solvent. In accordance with a second aspect of the present disclosure, a bimetallic Rh-based catalyst for use in producing sustainable aviation fuel from plastic waste is provided. The catalyst comprises Rh_2MoO_x supported on an Al-SBA-15 material, represented by $\text{Rh}_2\text{MoO}_x/\text{Al-SBA-15}$.

DESCRIPTION

[0010] The following description sets forth exemplary methods, parameters, and the like. The embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized, and structural and logical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0011] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0012] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0013] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance, e.g. within 10% of the specified value.

[0014] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0015] By “comprising” it is meant including, but not limited to, whatever follows the word “comprising”. Thus, use of the term “comprising” indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0016] By “consisting of” is meant including, and limited to, whatever follows the phrase “consisting of”. Thus, the phrase “consisting of” indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0017] The present disclosure relates to a highly selective catalytic method for producing sustainable aviation fuel (SAF) from plastic waste.

[0018] The term “plastic waste” as used herein refers to discarded, unused, or unwanted plastic material that has reached the end of its useful life and is no longer needed. This can include items such as plastic packaging, bottles, bags, containers, and other single-use plastic products that are disposed of after use. Plastics are made from a wide range of organic polymers including, but are not limited to, polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS), polyethylene terephthalate (PET), etc. In some preferred embodiments, the plastic waste is polypropylene (PP).

[0019] The term “sustainable aviation fuel” as used herein refers to hydrocarbons containing carbon ranging from C₆-C₁₆, with major range of products in C₈-C₁₆.

[0020] According to a first aspect, the catalytic method comprises subjecting plastic waste to hydrocracking under mild conditions in the presence of a catalyst to obtain a sustainable aviation fuel, wherein the mild conditions include heating the plastic waste at a temperature of less than 300°C, under 2×10^6 Pa (20 bar) of hydrogen pressure, and within 3 hours; and wherein the catalyst is a bimetallic Rh-based catalyst, Rh₂MoO_x, supported on an Al-SBA-15 material, represented by Rh₂MoO_x/Al-SBA-15.

[0021] The term “Al-SBA-15” as used herein refers to a type of mesoporous support that falls under the family of SBA (Santa Barbara Amorphous) mesoporous silicas, where aluminium (Al) is incorporated into the SBA-15 framework. In some embodiments, the Al-SBA-15 support has highly ordered pore structures with uniform pore sizes ranging from 2 to 30 nanometres.

[0022] The bimetallic Rh-based catalyst, Rh_2MoO_x , is a mixed-metal oxide catalyst composed of rhodium (Rh) and molybdenum (Mo). The value of “x” in Rh_2MoO_x can vary depending on the specific synthesis method and conditions used to prepare the catalyst. In some embodiments, the value of “x” ranges from 2 to 3.

[0023] In some embodiments, the sustainable aviation fuel comprises hydrocarbons with carbon ranging from C_6 - C_{16} , with major range of products in C_8 - C_{16} .

[0024] In some embodiments, the hydrocracking is performed in the absence of a solvent. Performing hydrocracking without a solvent helps to reduce operational costs and increase efficiency as there are no solvent waste to be disposed of after the generation of the sustainable aviation fuel by the method of the present disclosure.

[0025] In some embodiments, the catalyst, represented by $\text{Rh}_2\text{MoO}_x/\text{Al-SBA-15}$, has a metal loading ranging from 0.5 to 3 wt%, based on the total weight of the catalyst. In some embodiments, the amount of Rh (rhodium) and Mo (molybdenum) loaded onto the support material is in a ratio of 2:5.

[0026] In some embodiments, the plastic waste is a single source plastic selected from the group consisting of polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET). In some preferred embodiments, the plastic waste is polypropylene (PP).

[0027] The method of the present disclosure yields organic oil products comprising saturated hydrocarbons with carbon ranging from C_6 - C_{35} , achieving a relatively high yield of about 94% (Table 1, entry 2), together with gaseous products and solid residue. In some

embodiments, the method produces an average yield of about 83% w/w of sustainable aviation fuel with hydrocarbons falling within the C₆-C₁₆ range, with major range of products in C₈-C₁₆, from the plastic waste. The remaining organic oil products consist mainly of 6% of C₁₇-C₂₀ and 2% C₂₁-C₃₅ hydrocarbons in the motor oil range. The gaseous products produced by the method are composed of small hydrocarbon molecules (C₁-C₄) and unreacted hydrogen.

[0028] Unlike the conventional methods, the method of the present disclosure achieves a relatively higher yield of C₈-C₁₆ sustainable aviation fuel using mild reaction conditions. This is in contrast to some conventional methods that may require harsher conditions and longer reaction times to achieve similar results. The technology of the present disclosure has the potential to accelerate the 'greening' of air traffic, facilitating the transition to alternative, greener, and renewable aviation fuels. Additionally, it offers an alternative solution for managing plastics waste, contributing to the realisation of a 'zero waste' plan.

[0029] According to a second aspect of the present disclosure, a bimetallic Rh-based catalyst for use in producing sustainable aviation fuel from plastic waste is provided. The bimetallic Rh-based catalyst comprises Rh₂MoO_x supported on an Al-SBA-15 material, represented by Rh₂MoO_x/Al-SBA-15.

[0030] In some embodiments, the catalyst is prepared by mixing a solution containing ammonium molybdate tetrahydrate, ((NH₄)₆Mo₇O₂₄·4H₂O) with Al-SBA-15 and subjecting the mixture to rotavap to obtain a solid residue. The solid residue is dried before it is calcined in a furnace to obtain MoO_x/Al-SBA-15. A Rh(NO₃)₃ solution precursor is prepared and the MoO_x/Al-SBA-15 is added to the solution and mixed. The mixture is then subjected to rotavap to obtain a solid residue. The solid residue is dried before it is calcined in the furnace to obtain RhMoO_x/Al-SBA-15. The final active catalyst, Rh₂MoO_x/Al-SBA-15, is then obtained by the reduction of the solid catalyst under H₂ gas.

[0031] In some embodiments, the catalyst has a metal loading ranging from 0.5 to 3 wt% based on the total weight of the catalyst. This metal loading is several times lower than some catalysts known in the state of the art.

[0032] In addition, the catalyst of the present disclosure significantly reduces the reaction time by approximately 5 to 24 fold and lowers reaction pressure by 2 to 3 times compared to some catalysts known in the state of the art. The catalyst is reusable while maintaining high selectivity and yield of sustainable aviation fuel. Methane fuel is also produced during the conversion of the plastic waste to sustainable aviation fuel. The methane fuel can be used to generate the hydrogen gas required for the hydrocracking process, thus establishing a self-sufficient system for producing sustainable aviation fuel from plastic waste.

[0033] The catalyst and method of the present disclosure offer a significant breakthrough in the conversion of plastic waste into valuable fuels. With an impressive yield of approximately 83% w/w of sustainable aviation fuel derived from plastic waste, this technology holds promise for reducing plastic waste and contributing to a circular economy. Moreover, by shifting focus from crude oil and natural gas extraction to the production of aviation and gas fuels, this method represents a sustainable alternative in fuel production. The method also lowers the overall operating costs and streamlines production.

[0034] To facilitate a better understanding of the present disclosure, the following examples of specific embodiments are given. In no way should the following examples be read to limit or define the entire scope of the disclosure. One skilled in the art will recognize that the examples set out below are not an exhaustive list of the embodiments of this disclosure.

EXAMPLES

Example 1

[0035] Preparation of the catalyst, Rh₂MoO₈/Al-SBA-15

[0036] The catalyst, Rh₂MoO₈/Al-SBA-15, was prepared by the addition of ammonium molybdate tetrahydrate, ((NH₄)₆Mo₇O₂₄·4H₂O) (0.20 mmol) to 20 mL of deionized water in a

round bottom flask and stirred for 30 mins to fully dissolve the precursor. Al-SBA-15 (1g) was subsequently added to the solution and the mixture was stirred for 3 hours at room temperature. The mixture was then subjected to rotavap to remove the deionized water to obtain a solid residue. The solid residue was dried in an oven at 80 °C overnight. The dried solid was then calcined in a box furnace at 500 °C, 10 K/min for 3 hours to obtain MoO₃/ Al-SBA-15. Rh(NO₃)₃ (0.08 mmol) solution precursor was added to 20 mL of deionized water in a round bottom flask and stirred for 30 mins. MoO₃/ Al-SBA-15 (1g) was subsequently added to the solution and the mixture was stirred for 3 hours at room temperature. The mixture was then subjected to rotavap to remove the deionized water to obtain a solid residue. The solid was dried in the oven at 80 °C overnight. The dried solid was then calcined in the box furnace at 500 °C, 10 K/min for 3 hours to obtain RhMoO₃/ Al-SBA-15. The final active catalyst, Rh₂MoO₃/Al-SBA-15, was then obtained by the reduction of the solid catalyst under H₂ gas at 300 °C, 1 °C/min for 30 mins.

Example 2

[0037] Preparation of other catalysts

[0038] Other catalysts supported on SBA-15 were prepared in a similar manner as in Example 1. The catalysts were prepared by the addition of ammonium molybdate tetrahydrate, (NH₄)₆Mo₇O₂₄·4H₂O (0.20 mmol) to 20 mL of deionized water in a round bottom flask and stirred for 30 mins to fully dissolve the precursor. SBA15 (1g) was subsequently added to the solution and the mixture was stirred for 3 hours at room temperature. The mixture was then subjected to rotavap to remove the deionized water to obtain a solid residue. The solid residue was dried in the oven at 80 °C overnight. The dried solid was then calcined in the box furnace at 500 °C, 10 K/min for 3 hours to obtain MoO₃/ SBA-15. Rh(NO₃)₃ (0.08 mmol) solution precursor was added to 20 mL of deionized water in a round bottom flask and stirred for 30 mins. MoO₃/ SBA-15 (1g) was subsequently added to the solution and the mixture was stirred

for 3 hours at room temperature. The mixture was then subjected to rotavap to remove the deionized water to obtain a solid residue. The solid was dried in the oven at 80 °C overnight. The dried solid was then calcined in the box furnace at 500 °C, 10 K/min for 3 hours to obtain RhMoO_x/SBA-15. The final active catalyst, Rh₂MoO_x/SBA-15 was then obtained by the reduction of the solid catalyst under H₂ gas at 300 °C, 1 °C/min for 30 mins.

[0039] Other catalysts supported on LaP₃ were prepared in a similar manner as in Example 1. Ammonium molybdate tetrahydrate, ((NH₄)₆Mo₇O₂₄·4H₂O) (0.20 mmol) was added to 20 mL of deionized water in a round bottom flask and stirred for 30 mins to fully dissolve the precursor. Lanthanum phosphate (LaP₃) (1g) was subsequently added to the solution and the mixture was stirred for 3 hours at room temperature. The mixture was then subjected to rotavap to remove the deionized water to obtain a solid residue. The solid residue was dried in the oven at 80 °C overnight. The dried solid was then calcined in the box furnace at 500 °C, 10 K/min for 3 hours to obtain the MoO_x/LaP₃. Rh(NO₃)₃ (0.08 mmol) solution precursor was added to 20 mL of deionized water in a round bottom flask and stirred for 30 mins. MoO_x/LaP₃ (1g) was subsequently added to the solution and the mixture was stirred for 3 hours at room temperature. The mixture was then subjected to rotavap to remove the deionized water to obtain a solid residue. The solid residue was dried in the oven at 80 °C overnight. The dried solid was then calcined in the box furnace at 500 °C, 10 K/min for 3 hours to obtain RhMoO_x/LaP₃. The final active catalyst, Rh₂MoO_x/LaP₃ was then obtained by the reduction of the solid catalyst under H₂ gas at 300 °C, 1 °C/min for 30 mins.

Example 3

[0040] Converting polypropylene (PP) waste into sustainable aviation fuel (SAF)

[0041] The hydrocracking of polypropylene (PP) waste was performed in a 160 mL Parr autoclave with an overhead mechanical stirrer attached to an impeller. PP (approx. 0.9 – 1.1 g) was added to the catalyst, Rh₂MoO_x/Al-SBA-15 (approx. 0.9 – 1.1 g) and was subjected to three cycles of purging with argon and H₂ gas. The Parr reactor was then pressurized with H₂

(20 bar) and heated at 300 °C for 3 hours with stirring. The reactor was allowed to cool slowly, and the pressure difference was noted before the gas in the headspace of the reactor was collected in a gas bag. 20 mL of dichloromethane (DCM) was added to the crude mixture and the liner was washed with DCM to prevent any loss of oil product. The resulting mixture was then filtered to remove the solid residue. The solid residue was dried in an oven at 70 °C overnight. The solid residue was subjected to pyrolysis gas chromatography-mass spectrometry analysis to obtain the distribution of hydrocarbons. The gas collected was analyzed by GC-FID and GC-TCD for quantification. The clear liquid filtrate was subjected to rotavap to remove all DCM present to obtain a colorless oil product and the final mass of the oil was recorded. A known quantity of internal standard, octacosane (avg. 0.01 mmol) was added to the oil mixture (0.2-0.3 g) in 3 mL of DCM. The oil product was subsequently analysed by GC-MS, GC-FID, pyrolysis gas chromatography-mass spectrometry and high temperature gel Permeation chromatography (HT-GPC). These procedures were repeated using the other catalysts. The results obtained are as shown in Table 1.

[0042] Table 1: Catalytic conversion of polypropylene

Entry	Catalyst	Conversion (%)	Yield (%)		
			Gas	Oil	Solid Residue
1	Rh1MoO ₃ /Al-SBA-15	100	78	22	0
2	Rh2MoO ₃ /Al-SBA-15	96	2	94	4
3	RhMoO ₃ /Al-SBA-15-s	98	26	72	2
4	Rh2/Al-SBA-15	92	38	54	8
5	Rh1MoO ₃ /SBA-15	100	38	62	0
6	Rh2MoO ₃ /SBA-15	80	10	70 ¹	20
7	Rh1/SBA-15	100	51	49	0
8	Rh2/SBA-15	91	7	84 ¹	9
9	Rh2MoO ₃ /LaP ₃	89	11	78	11
10	Rh2/LaP ₃	91	36	55	9
11	Rh2MoO ₃ /Al-SBA-15 ²	89	19	71	11

¹ the oil is mainly in the range of >C35

² the ratio of catalyst in entry 11 and entry 2 is 1:2 (i.e. the amount of catalyst added to entry 11 is half the amount of entry 2).

[0043] The reaction conditions employed for converting the plastic waste, polypropylene (PP) into SAF in the examples described hereinabove include heating the plastic waste at a temperature of less than 300°C, under a hydrogen pressure of 2×10^6 Pa (20 bar), and within 3 hours. The results in Table 1 show that the use of Rh₂MoO₈/Al-SBA-15 as the catalyst in the hydrocracking process can achieve a relatively high conversion rate (96% and 89%) and a relatively high yield of oil products (94% and 71%) in the range of C₆-C₃₅. The yield of SAF in the range of C₆-C₁₆ makes up an average of about 83% w/w of SAF, while the remaining consists mainly of 6% of C₁₇-C₂₀ and 2% C₂₁-C₃₅ hydrocarbons in the motor oil range. This is one of the highest yields towards the selective production of C₆-C₁₆ SAF among some of the methods known in the state of the art which require much harsher reaction conditions and longer reaction time to achieve similar results.

[0044] Although embodiments of the invention have been shown and described, the invention is not limited to the described embodiments. Instead, it would be appreciated by those skilled in the art that various modifications and variations can be made to the embodiments of the invention without departing from the scope of the invention, the scope of which is set forth in the following claims.

Claims

1. A catalytic method of producing sustainable aviation fuel from plastic waste, the method comprising:

subjecting plastic waste to hydrocracking under mild conditions in the presence of a catalyst to obtain a sustainable aviation fuel,

wherein the mild conditions include heating the plastic waste at a temperature of less than 300°C, under 2×10^6 Pa of hydrogen pressure, and within 3 hours; and

wherein the catalyst is a bimetallic Rh-based catalyst, Rh₂MoO_x, supported on an Al-SBA-15 material, represented by Rh₂MoO_x/Al-SBA-15.

2. The catalytic method of claim 1, wherein the sustainable aviation fuel comprises hydrocarbons with carbon ranging from C₆-C₁₆.

3. The catalytic method of claim 1, wherein the hydrocracking is performed in the absence of a solvent.

4. The catalytic method of claim 1, wherein the catalyst has a metal loading ranging from 0.5 to 3 wt% based on the total weight of the catalyst.

5. The catalytic method of claim 1, wherein the plastic waste is a single source plastic selected from the group consisting of polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET).

6. The catalytic method of claim 1, wherein the method produces an average of 83% w/w of sustainable aviation fuel from the plastic waste.

7. A bimetallic Rh-based catalyst for use in producing sustainable aviation fuel from plastic waste, the catalyst comprising Rh_2MoO_x supported on an Al-SBA-15 material, represented by $\text{Rh}_2\text{MoO}_x/\text{Al-SBA-15}$.

8. The catalyst of claim 7, wherein the catalyst has a metal loading ranging from 0.5 to 3 wt% based on the total weight of the catalyst.