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Evaluation methods and research progresses in bio-oil storage stability

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ABSTRACT

Bio-oil is the liquid product of the fast pyrolysis of biomass. Recently, bio-oil has gained increasing attention for its direct use in combustion within boilers and furnaces as well as its use in automobiles and chemical materials after refining. Unfortunately, the composition of bio-oil is very complex. Aging occurs during storage, which leads to obvious changes in the physical and chemical properties of the oil. The poor storage stability of bio-oil restricts its extensive applications as a key renewable energy alternative. Viscosity and average molecular weight, as well as water and solid content can measured to determine changes in bio-oil. In this article, the testing parameters and technologies used for examining bio-oil stability and research progress in the field of bio-oil stability are reviewed. Emphasis is placed on thermal and oxidation stability. Scientific and technical developments towards improving bio-oil stability are also discussed. Furthermore, important aspects for consideration when developing experimental plans for bio-oil upgrades are examined. It also points out challenges to success with bio-oil upgrading in the future.

Contents

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1. Introduction

Biomass is the well known renewable energy resource which has advantages of being environmentally friendly, available in large reserves, and CO_2/green house gas neutral [1,2]. Fast pyrolysis of biomass is a thermo-chemical conversion process under anaerobic conditions at intermediate temperatures (about 500 °C) and produces liquid product (bio-oil), solid product (biochar), and gaseous product (fuel gas) [3]. It has been recognized as one of the most important methods for biomass utilization [4].

In recent years, fast pyrolysis of biomass for bio-oil production has received increasing attention [5,6]. Self-heating fast pyrolysis using straw as the raw material determined the yield and calorific values to be 50–55% and 15–16 MJ/kg for bio-oil and 28–33% and 18–20 MJ/kg for biochar, respectively; for forestry waste, bio-oil has a yield of 60–70% and calorific value of 16–17 MJ/kg, while biochar has a yield of 20–25% and calorific value of 20–22 MJ/kg, respectively [7,8]. Bio-oil is high in energy density, low in sulfur and nitrogen content, and is easy to store, transport, and utilize [2]. For these reasons, bio-oil is considered to be a clean fuel which can be directly used as fuel for combustion in boilers and furnaces [9]. Once it is refined, bio-oil can also be used as engine fuel and chemical materials [10–12]. In recent years, the prices of fossil fuel oils have risen with the increasing prices of crude oil. These increases have led to reduced oil resources of industrial burning oil. Hence, the market prospects of bio-oil obtained from the fast pyrolysis of biomass as fuel for industrial furnaces and oil burning boilers are promising [13]. From the long term perspectives, bio-oil has a broader market prospect as vehicle fuels or chemical materials to produce basic chemicals [14].

Although bio-oil is considered as a key renewable energy alternative, it has not been widely used due to some negative properties. First of all, there are hundreds of compounds in bio-oil and thus it is different to separate and refine [15]. Secondly, unlike fossil fuels, bio-oil exhibits characteristics such as high oxygen concentration, high moisture content, high viscosity, high acidity, and low calorific value. But most of all, the stability of bio-oil is very poor, which lead to obvious changes in physical and chemical properties of bio-oil [16], and difficult utilization of bio-oil in existing devices [17–19]. During storage, the aging of bio-oil not only deteriorates the quality of bio-oil but also influences the refining of bio-oil and its extracted chemicals [20–23]. In terms of combustion, an aging bio-oil will lead to more serious abrasion, corrosion, carbon accumulation and poor working performance of gas turbine. After long-term placement, the originally homogeneous bio-oil is even divided into two or three mutually insoluble components. In addition, bio-oil has low pH values and contains solid mixtures [24]. These qualities further deteriorate the stability of bio-oil. Hence, the properties of bio-oil, especially the storage stability, need to be researched and improved.

Storage stability of bio-oil is a crucial factor of bio-oil and it has a significant effect on bio-oil application. Recently, numerous studies have been carried out on bio-oil stability. These previous studies involved several important aspects: (i) parameters used for the evaluation of bio-oil stability, which include water content [25], viscosity [18], solid content [26] and average molecular weight [27]; (ii) evaluation methods for storage stability of bio-oil, which mainly include thermoanalysis technologies [28], Fourier transform infrared spectroscopy (FTIR) [29], and gas chromatography/mass spectrometry (GC/MS) [30]; (iii) aging mechanism of bio-oil [31]; and (iv) methods to improve bio-oil stability, including biomass drying [32], ash and char removing [33], adding solvent [34], emulsification [35], adding antioxidant [36], catalytic cracking [37], catalytic hydrogenation [38], and catalytic esterification [39]. These previous studies achieved remarkable advances in understanding the storage stability of bio-oil. However, the thermal and oxidation stability of bio-oil, especially the scientific and technical developments towards improving bio-oil stability, have not been fully reviewed. As far as we know, there is no review paper that focused on the storage stability of bio-oil reported in the literature in the last 10 years. Due to lots of newest paper published, summarizing these new papers and data is essential in order to better provide the information for the use of bio-oil.

Therefore, this paper reviews the research progress of bio-oil stability, with emphasis on thermal and oxidation stability. Additionally, methods for evaluation and technologies used for improvement of bio-oil are discussed. It also points out challenges to success with bio-oil upgrading in the future.

2. Basic properties of bio-oil

2.1. Physical properties

Bio-oil is a flowing liquid that is sepia in color, opaque, sticky and pungent. Table 1 shows the basic properties of bio-oil and fossil fuel [40]. Compared with fossil fuels, bio-oil has the

Table 1
Basic property of bio-oil and fossil fuel [20].

Fuel property	Bio-oil	Crude oil	Heavy fuel oil	Diesel	Gasoline
Water (%)	20～30	0.3	0.1	0.1	0.025
Solids /%	＜1		0.2～2.5	＜0.5	–
Ash (%)	0.1～0.5	0.02～0.07	＞0.3	＜0.01	–
C (%)	32～50	84～87	85～86	85～86	84～88
H (%)	8～11	11～14	12.5～14	13～15	12～16
N (%)	＜0.4	0.02～1.7	0.2	0.1	0.1
O (%)	45～60	0.08～1.82	1	–	–
S (%)	＜0.3	0.06～2	＞1	0.2～0.5	0.08
Stability	Unstable	–	Steady	Steady	Steady
Viscosity (cSt)	10～90 (40 °C)	20～40 (40 °C)	20～200 (80 °C)	1.6～5.8 (40 °C)	0.6～0.7 (40 °C)
Density (g mL^{-3})	1.2	0.7～1.0	＜0.98	0.85	0.7～0.8
Flash point (°C)	70～100	−10～28	＜130	40～55	−50～−40
HHV (MJ kg^{-1})	15～18	41～45	39～41	40～46	46
pH	2.0～4.0	–	–	--	–