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Preparation of bio-bitumen by bio-oil based on free radical polymerization and production process optimization

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ABSTRACT

Bio-oil produced during the production of biodiesel is a burden to the environment. Recycling and utilization of bio-oil as a substitute for pavement bitumen can help to build an environmentally-friendly and clean infrastructure. In this study, the bio-bitumen was prepared by bio-oil based on free radical polymerization. Different kinds of bio-bitumen products were produced by reacting bio-oil with an initiator and an accelerator solution at different reaction conditions. The orthogonal experimental method was employed to determine the optimal bio-bitumen production process by evaluating the indices of viscosity, rutting factors and fatigue factors. The test results show that the optimal mass proportions of bio-oil:initiator:accelerator solution is 100:1:2. Materials with these mass proportions should react at 100 °C for 2 h to yield the best bio-bitumen product. This kind of bio-bitumen product can be considered as a promising substitute for traditional petroleum bitumen.

1. Introduction

As a residue from the crude oil refining process, traditional petroleum bitumen is widely used in the pavement construction industry. However, gradually decreasing crude oil reserves and increasingly strict environmental regulations have triggered the search for sustainable methods to produce bitumen substitutes. One of the promising methods proposed by researchers is to prepare bitumen substitutes from renewable and environmentally friendly bio-mass materials, the final product is also known as bio-bitumen (Wen et al., 2012; Fini et al., 2013; Hill et al., 2016).

Among current researches, bio-oils derived from bio-mass materials are commonly utilized to produce bio-bitumen. Bio-oils can be used as modifiers, extenders, and perfect substitutes for bitumen based on its properties (Raouf and Williams, 2010), which significantly depend on the sources and production process (Zhang et al., 2015; Yang and You, 2015). For instance, the bio-oil derived from swine manure can improve the low-temperature properties while decrease the high-temperature grade of base bitumen (Fini et al., 2012). However, the bio-oil generated from waste wood resources can improve the high-temperature performance while sacrifice the medium and low-temperature performance of base bitumen (Yang et al., 2013). Besides, Yousefi et al. (2000) found that the bio-oil obtained from used-tire can also improve the low-temperature properties of base bitumen. Chailleux et al. (2012) produced a kind of bio-oil from microalgae, which showed thermo-dependent behavior comparable to asphalt. As for the production process of bio-oil, the commonly used methods are pyrolysis (Mohan et al., 2006) and liquefaction (Aude et al., 2015). In addition, bio-oils can also refer to some renewable waste oils, such as waste cooking oil (Sun et al., 2016a), waste lubricating oil (Villanueva et al., 2008), waste engine oil (Rubab et al., 2011), and so on.

China's food industry produces more than 5 million tons of waste cooking oil every year, which is normally used to produce biodiesel. However, about 10%–20% of by-products (bio-oil) can be obtained during the production of biodiesel. Although this kind of bio-oil can be used to refine glycerin, the high refining cost prevents its extensive use. In fact, most bio-oil is simply kept in factories, occupying massive land resources. The leakage risk of these sites is a potential detriment to the clean and environmentally-friendly material recycling system.

There are many methods to prepare satisfactory bio-bitumen using bio-oil. The most common method is to modify base bitumen with bio-oil directly (Villanueva et al., 2008; Sun et al.,

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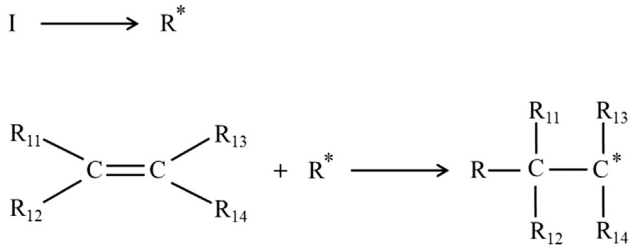

Fig. 1. Schematic presentation of chain initiation.

2016b; Yang et al., 2017), but the content of the bio-oil is usually very limited because of the poor high-temperature performance of bio-oil. Bio-oil can also be treated to reduce unfavorable components before being used as a modifier of base bitumen, which improves the performance of final bio-bitumen products (Zhang et al., 2017). In addition, bio-oil can also be modified by polymers (Peralta et al., 2012) or mixed with other materials, such as hard bitumen particles and resin (Sun et al., 2017), to obtain satisfactory bio-bitumen, which can be used as the perfect substitute for traditional petroleum bitumen.

Most researchers, however, have focused on the physical method to prepare bio-bitumen using bio-oil, such as physical mixing or simple modification. Few have investigated the chemical method to prepare bio-bitumen using bio-oil. This method has the potential to produce better bio-bitumen owing to the strong chemical bonds in the final product. Additionally, it is also meaningful to investigate the production process of bio-bitumen, because the production process has significant influence on the performance of the final product. In this paper, a chemical method is introduced to prepare bio-bitumen using bio-oil, and the production process of bio-bitumen is also optimized based on the orthogonal experimental method.

2. Reaction mechanisms

Free radical polymerization occurs in the production process of high molecular weight bio-bitumen by low molecular weight bio-oil. The total process of free radical polymerization entails the elementary reactions of chain initiation, chain growth, and chain transfer or chain termination. These elementary reactions constitute the microscopic process of free radical polymerization. The free radical polymerization procedure is described below.

First, the initiator (I) decomposes into primary free radical R^*, which undergoes an additional reaction with the carbon–carbon double bond in a monomer to generate a monomer free radical. This process is called chain initiation (see Fig. 1).

Second, the monomer free radical reacts with the carbon–carbon double bonds in other monomers, continuously and rapidly, to increase the chain (see Fig. 2). The active center is always at the end of the chain.

Finally, the active chain transfers the activity to the monomer or solvent M and becomes stable, which process is called chain transfer. The active chain can also terminate itself to be an inactive polymer, which process is called chain termination (see Fig. 3).

3. Materials and methods

The details of the experimental materials, the preparation process of bio-bitumen, and corresponding performance evaluation methods are shown in this section.

3.1. Bio-oil

Bio-oil, a black oily liquid, is the by-product in the process of refining waste cooking oil for biodiesel. The bio-oil used in this research is the same as the one used in previous research. The detailed basic properties of bio-oil can be found in Sun et al. (2016a).

3.2. Initiator

The initiator used for polymerization in this research is tert-butyl peroxybenzoate (TBPB), whose Chemical Abstracts Service (CAS) number is 614-45-9. It is a clear, colorless to slightly yellow,

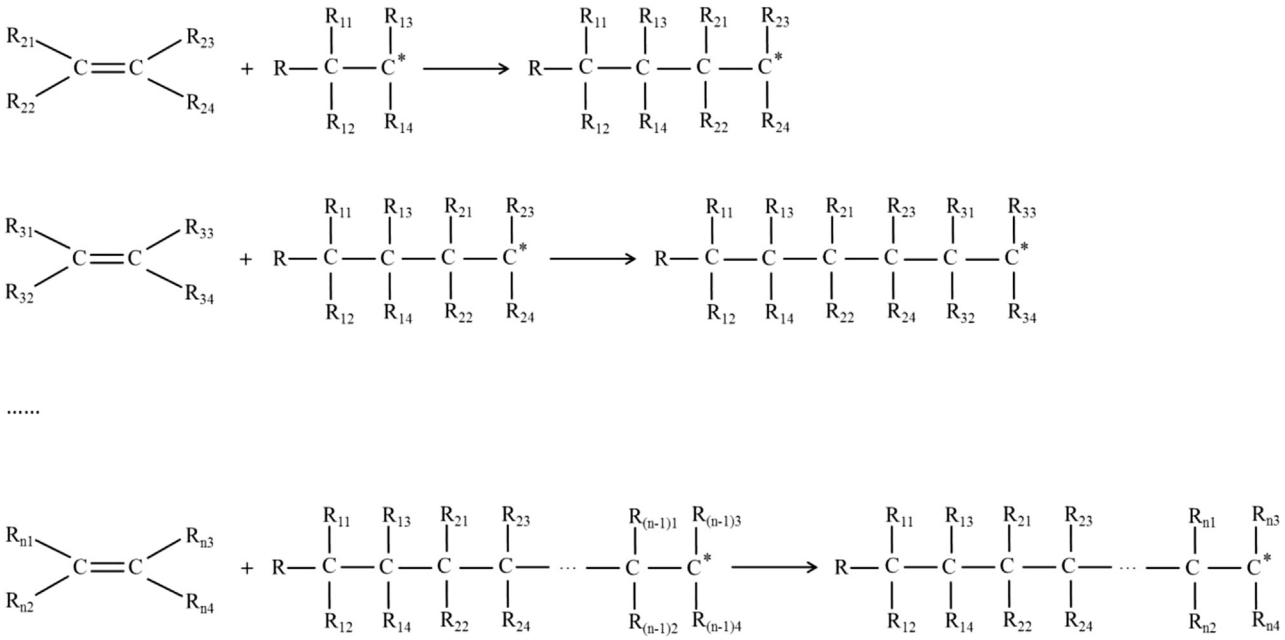

Fig. 2. Schematic presentation of chain growth.