# Study on oxidative stabilities of waste cooking oil biodiesel

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## Abstract

The present work investigates the oxidation stabilities of waste cooking oil biodiesel (WCOB). Physical properties and chemical composition of WCOB, including density, kinematic viscosity, acid number (AN), and induction period (IP), were measured. The analysis showed that WCOB contains over 71% unsaturated fatty acid methyl esters (UFAME). The long-term storage stability was studied up to 24 weeks closed storage by holding samples at room temperature. NB/SH/T 0825-2015 tests were conducted to investigate oxidation processes of WCOB. An extended the long-term storage method was also employed to investigate the influence of oxidation time on stability. The study showed that approximately 70% of the UFAME contain bis-allylic sites which highly affect the WCOB stability. Oxidation slightly increased density, significant impacts on fuel properties, such as increased kinematic viscosity and AN, decreased IP.

## Keywords

Biodiesel, Oxidation stability, Waste cooking oil.

## 1. Introduction

Biodiesel (fatty acid methyl ester, FAME) has increased due to the diminishing oil reserves and the environmental consequences of exhaust gases from petroleum-fueled engines. In China, urban areas every year usually produce a lot of hutch garbage, which can be extracted waste cooking oil about more than 500 ten thousand tones [1]. It relieves the problem of biodiesel raw material shortage that using waste cooking oil to prepare biodiesel, which achieved the resource waste harmless treatment and avoided harm of waste cooking oil at the same time.

Stability is one of the important criteria concerning fuel properties. The stability of biodiesel is lower than common diesel fuel owing to the presence of unsaturated bonds in the molecules inherited from its parent feedstock. This susceptibility to oxidation has significant impact on the diesel quality during long-term storage and handling. Oxidation stability of biodiesel has been a subject of considerable research for last two decades. The general oxidation of unsaturated fatty acid methyl ester (UFAME) involves two types: autoxidation and photooxidation [2-3]. Oxidation starts at the allylic positions to double bonds. Therefore, the fatty acid composition of the ester, especially the position of and the number of allylic and bis-allylic methylene moieties adjacent to the double bond, determines the rate of oxidation [4-5].

In this article, the physicochemical properties and chemical composition of commercial biodiesel derived from waste cooking oil produced by Nantong BIOLUX Bioenergy Protein Feed Co. Ltd.. are reported. Additionally, the influence of oxidation on fuel physicochemical properties and oxidation stability, such as density, kinematic viscosity, acid number (AN), and induction period (IP), were also investigated using national standard methods.

# 2. Experimental

## 2.1 Materials

Waste cooking oil biodiesel (WCOB) was obtained from Nantong BIOLUX Bioenergy Protein Feed Co. Ltd.

## 2.2 Chemical compositions

WCOB was determined by gas chromatography-mass spectrometer (GC-MS) (Finnigan, Trace MS, FID, USA), equipped with a capillary column (DB-WAX, 30 m × 0.25 mm × 0.25μm). The carrier gas was helium (0.8 mL/min). The sample injection volume was 1μL. Temperature program was started at 160 °C, staying at this temperature for 0.5 min, heated to 215 °C at 6 °C /min, then heated to 230 °C at 3 °C /min, staying at this temperature for 13 min.

## 2.3 Properties

The density of biodiesel samples at temperatures according to the GB/T 13377-2010 method. The kinematic viscosity was measured in SYP2007-7 the kinematic viscosity tester (shanghai boli, China) following the GB/T 265-88 procedures. GB/T 7304-2014 was also employed to measure the acid number (AN) of the biodiesel samples.

## 2.4 Oxidative stabilities

Oxidative stability was evaluated using a Rancimat 873 (Metrohm), following the standard NB/SH/T 0825-2015.

# 3. Results and Discussion

## 3.1 Chemical composition

The GC-MS scan of WCOB had 13 dominant peaks ranging in retention time from 1 to 18 min, as shown in Fig. 1. The main components of WCOB was shown in Table 1.

From Table 1, it can be seen that the mass fractions of SFAMEs and UFAMEs were 27.63% and 71.81%, respectively. The amount of polyunsaturated fatty acid methyl esters (PUFAMEs) with accounts for over 32% of the biodiesel, which highly influences the stability of the fuel sample. In Fig.2, the positions in the C18:1, C18:2 and C18:3 present in WCOB that are vulnerable to oxidation are highlighted by a circle with dotted lines. The allylic and bis-allylic methylene moieties are the most susceptible to oxidation as a result of the radical chain reaction.

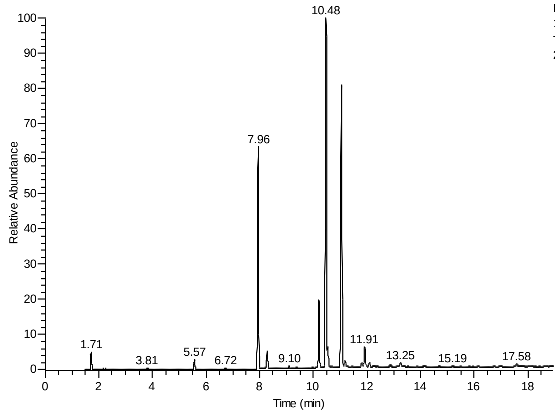
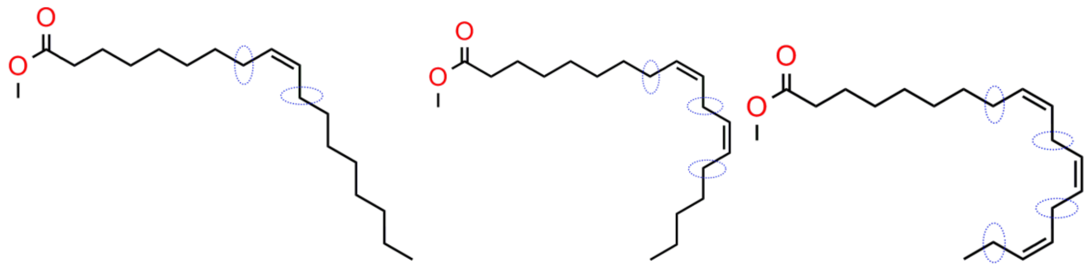



Fig. 1 GC/MS chromatogram of WCOB

Table 1 The main chemical compositions of WCOB

| WCOB | $C_{12:0}$ | $C_{14:0}$ | $C_{16:0}$ | $C_{18:0}$ | $C_{20:0}$ | $C_{22:0}$ | $C_{16:1}$ | $C_{18:1}$ | $C_{20:1}$ | $C_{22:1}$ | $C_{18:2}$ | $C_{20:2}$ | $C_{18:3}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (w)% | 0.09 | 0.83 | 20.66 | 5.78 | 0.19 | 0.08 | 1.64 | 36.77 | 0.55 | 0.43 | 29.41 | 0.10 | 2.91 |

$C_{m:n}$ is shorthand of fatty acid methyl ester. *m* is the number of carbon atom in fatty acid group. *n* is the number of double bond.




C18:1 C18:2 C18:3

Fig. 2 Unsaturated fatty acid methyl ester biodiesel molecules

From Table 1, it can be seen that the mass fractions of SFAMEs and UFAMEs were 27.63% and 71.81%, respectively. The amount of polyunsaturated fatty acid methyl esters (PUFAMEs) with accounts for over 32% of the biodiesel, which highly influences the stability of the fuel sample. In Fig.2, the positions in the C18:1, C18:2 and C18:3 present in WCOB that are vulnerable to oxidation are highlighted by a circle with dotted lines. The allylic and bis-allylic methylene moieties are the most susceptible to oxidation as a result of the radical chain reaction.

### 3.2 Properties

The Table 2 lists the properties of the WCOB. The four measured properties of WCOB meet the GB/T 20828-2015 specification,—kinematic viscosity (*v*) in the range of 1.9–6.0 $mm^2s^{-1}$ at 40 °C, acid value (*AV*) < 0.5 mg of KOH/g and induction period (*IP*) > 6.0 h at 110 °C.

Table 2 The properties of WCOB

| Biodiesel | $\rho$ at 20 °C ($gcm^{-3}$) | *v* at 40 °C ($mm^2s^{-1}$) | *AN* (mg of KOH/g) | *IP* at 110 °C (h) |
|---|---|---|---|---|
| WCOB (as-purchased) | 0.8812 | 4.40 | 0.24 | 6.12 |
| WCOB (12 weeks) | 0.8816 | 4.53 | 0.29 | 1.32 |
| WCOB (24 weeks) | 0.8819 | 4.61 | 0.33 | 0.40 |

### 3.3 Oxidation stability

A fuel's storage stability is highly affected fuel oxidative and thermal stabilities. WCOB samples was subjected to long-term storage tests, for 24 weeks with replicated analyses occurring at 0, 12, and 24 weeks. The adherent insoluble was formed in the biodiesel sample, and increased with storage time. The physicochemical properties of the biodiesel were also affected by the long-term storage as shown in Table 2. The density, kinematic viscosity, and acid value all increased after 24 weeks of storage. The kinematic viscosity and AV of the stored samples remained within GB/T 20828-2015 specifications. But the IP was reduced from 6.12 h to 1.32 h and 0.40 h, and not meeting the GB/T 20828-2015 specification.

Table 3 WCOB composition change (w)%

| FAME | $C_{16:0}$ | $C_{18:0}$ | $C_{18:1}$ | $C_{18:2}$ | $C_{18:3}$ |
|---|---|---|---|---|---|
| 0 weeks | 20.66 | 5.78 | 36.77 | 29.41 | 2.91 |
| 12 weeks | 28.07 | 8.73 | 25.72 | 7.35 | 0 |
| 24 weeks | 43,91 | 12.28 | 23.36 | 0 | 0 |

The influence of oxidation time on biodiesel composition was also investigated. Table 3 shows the composition change of the five major components, i.e. methyl palmitate ($C_{16:0}$), methyl stearate ($C_{18:0}$), methyl oleate ($C_{18:1}$), methyl linoleate ($C_{18:2}$), and methyl linolenate ($C_{18:3}$), after the biodiesel samples for 12 and 24 weeks. As expected, the composition of unsaturated esters, i.e. $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$ decreased with oxidation time owing to the breaking of double bonds. The mass fractions of $C_{18:2}$ and $C_{18:3}$ were reduced to 0% after 12 and 24 weeks, respectively. In addition, the degradation rates of $C_{18:2}$ and $C_{18:3}$ were faster than $C_{18:1}$. This demonstrates that polyunsaturated esters are more susceptible to oxidation than monounsaturated esters owing to the presence of additional bis-allylic methylene groups.

## 4. Conclusion

The influence of long-term storage and oxidation on properties of WCOB was investigated by monitoring density, viscosity, AN, and IP. WCOB consists of five primary compounds, i.e. $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$. UFAME account for >71% and approximately 70% of the UFAME contain bis-allylic sites which highly affect WCOB stability. Oxidation slightly increased density, significant impacts on fuel properties, such as increased kinematic viscosity and AN, decreased IP.

## Acknowledgements

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