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## Laboratory Analytical Procedure (LAP)

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*National Renewable Energy Laboratory*

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**Technical Report**  
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## 1. Introduction

- 1.1 This laboratory analytical procedure covers the accelerated aging of fast pyrolysis bio-oils. Bio-oils undergo reactions that result in physical and chemical changes over time [1]. These changes typically result in an increase in molecular weight, decrease in some functional groups such as carbonyls, and an increase in viscosity; additionally, the aging process often leads to phase separation [2,3,4]. Studies have shown [2] that accelerated aging of bio-oils using this method closely mimics room temperature aging for long periods of time (3+ years).

## 2. Scope

- 2.1 This procedure has been developed for the accelerated aging of fast pyrolysis bio-oils. Fast pyrolysis bio-oils are more reactive than other bio-oils (e.g., catalytic fast pyrolysis) and undergo aging much more rapidly. Therefore, this procedure should only be used for fast pyrolysis bio-oil samples.

## 3. Terminology

- 3.1 *Bio-oil* – The crude liquid product of converting solid biomass into a liquid via fast pyrolysis or other thermochemical conversion process.
- 3.2 *Pyrolysis* – Chemical decomposition of organic materials by heating in the absence of oxygen.
- 3.3 *Fast Pyrolysis (FP)* – Pyrolysis conducted with rapid heating and short residence time; typically, less than 10 seconds.
- 3.4 *Catalytic Fast Pyrolysis (CFP)* – Fast pyrolysis conducted in the presence of a catalyst designed to perform partial deoxygenation.
- 3.5 *Bio-oil aging* – The chemical and physical changes that result during the storage of bio-oil.
- 3.6 *Accelerated bio-oil aging* – Heating of bio-oil to accelerate the rate of chemical and physical changes. Accelerated aging results are then correlated to long-term aging at room temperature. In this method, accelerated aging is performed at 80°C.

## 4. Significance and Use

- 4.1 Accelerated aging of bio-oils is an important measure of the stability of bio-oils and this method can be used to gauge how a sample has changed, or will change, with varying times of storage at room temperature. This type of information would be very useful in many different industrial processing strategies and will inform decision making around both the processability of the bio-oil at different storage times, as well

as how to run the process itself. This accelerated aging protocol correlates to 1-3 months of storage at room temperature for typical fast pyrolysis bio-oils [2].

- 4.2 This method uses total carbonyl content (measured by carbonyl titration) to track bio-oil aging. While viscosity has often been commonly used to track bio-oil aging, it has recently been shown that carbonyl content is a better metric [2]. First off, carbonyl titration has lower variability than does the viscosity measurement. Additionally, carbonyl titration can be applied to samples that have phase separated (a common occurrence during aging) while the viscosity measurement cannot.
- 4.3 The carbonyl titration method employed is available as a separate Laboratory Analytical Procedure [6] and as an ASTM Standard Test Method [7]. Additionally, a video tutorial of this titration method is available [8].

## 5. Interferences

- 5.1 Fast pyrolysis bio-oils can phase separate during aging at elevated temperatures. A phase separated sample maybe homogenized by heating in a 50°C oven for 15 minutes, followed by agitation to ensure complete mixing of the two-phase sample.
- 5.2 Bio-oils are known to undergo aging processes both at room temperature as well as in cold storage [2]. Due to this, analyses on bio-oil samples should be performed as quickly as possible following production. Even samples stored at -20°C may show significant changes within 6 months of production. Users must be mindful that samples that have aged may not be representative of the original bio-oil product.
- 5.3 Bio-oils contain volatile compounds. Sealing of the vial during heating and measuring for weight loss are critical. Excess weight loss during heating will result in an inaccurate carbonyl measurement.

## 6. Apparatus

- 6.1 Analytical balance accurate to 1 mg.
- 6.2 Oven capable of maintaining temperature control of 80°C±0.5°C.

## 7. Reagents and Materials

### 7.1 Reagents

- 7.1.1 Please see reference [6] for reagents needed for carbonyl titration.

### 7.2 Materials

- 7.2.1 10 mL glass bottles with caps capable of being heated to 80°C (DURAN® GL 25 laboratory glass bottle, clear, with cap or equivalent).
- 7.2.2 Please see reference [6] for materials needed for carbonyl titration.

## 8. Environmental Safety and Health Considerations and Hazards

- 8.1 Follow all applicable chemical handling procedures.

## 9. Sampling, Test Specimens, and Test Units

- 9.1 Bio-oil should be allowed to reach room temperature and thoroughly homogenized to obtain a representative sample.
- 9.2 Exposure to oxygen and heat should be minimized to prevent sample degradation prior to analysis.

## 10. Procedure

### 10.1 Bio-oil aging

- 10.1.1 Measure total carbonyl content in triplicate following reference [6]. Record the average of three measurements as the initial carbonyl content ( $C_{initial}$ ) prior to accelerated aging.
- 10.1.1 Dry 10mL bottles and caps at 100°C overnight. Cool to room temperature.
- 10.1.2 Pour 5g±0.5g into the bottle and record the weight. Prepare each sample in triplicate.
- 10.1.3 Tightly seal and place bottles in 80°C oven.
- 10.1.4 After 2 hours, remove bottles from oven.
- 10.1.5 Allow samples to cool to room temperature. Weigh the samples and reject any weight losses over 0.25%.
- 10.1.6 Measure total carbonyl content following reference [6]. Record the average of three measurements as the aged carbonyl content ( $C_{aged}$ ) after accelerated aging.

## 11. Calculations

### 11.1 Calculate the aging index

- 11.1.1 Aging index =  $(C_{initial} - C_{aged}) / C_{initial} * 100\%$

- 11.2 The aging index has been calculated for a broad range of fast pyrolysis bio-oils, see further details in reference [2]. Typical results are between 6-14%, and correlate to 1-3 months of storage at room temperature.

## 12. Report Format

- 12.1 Report initial carbonyl content ( $C_{initial}$  in mol/kg), aged carbonyl content ( $C_{aged}$  in mol/kg), and the aging index (%).

## 13. Precision and Bias

- 13.1 To be determined by an interlaboratory study.

## 14. Quality Control

- 14.1 Evaluate the percent relative standard deviation (RSD) of triplicate sample preparations (10.1.1 and 10.1.6). If triplicate analyses result in an  $RSD > 10\%$  this may indicate poor homogeneity of the sample, or an error during titration. Re-analysis of the sample is suggested to determine whether an error occurred during sample preparation or titration. If poor homogeneity of samples is suspected, it is recommended that each sample be prepared in triplicate and an average value taken.

## 15. References

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