China Steel Technical Report, No. 27, pp.78－82, (2014)

An Emulsification Method of Bio-oils in Diesel

CHENG-TING HSIEH, PEI-HSUN LIN and JHY-HSIUNG LAI

New Materials Research & Development Department
China Steel Corporation

Bio-oil is an important alternative source of energy for the steel mill to reduce CO_2 emissions. In order to replace fossil fuel with bio-oil, this study develops an emulsification method to emulsify various bio-oils in diesel. The emulsification method developed in this work includes selection of the emulsifier, setting of emulsion composition, and the procedure of emulsion production. The core of the emulsification method is an equation which describes the relationship between the gross heating values of the bio-oils and the optimal HLB values of emulsifiers. The equation is helpful for the selection of the emulsifier. For the setting of the emulsion composition, this work found that the concentration of the emulsifier should be increased for emulsifying the bio-oil with a higher gross heating value in diesel, or the mixture of bio-oil and diesel with a higher concentration of bio-oil. The homogeneity is checked irregularly by detecting the gross heating value, the moisture, and the viscosity of the emulsion. The tracking results of the emulsion homogeneity showed the emulsification method developed in this work is feasible to produce a stable and homogeneous emulsion.

Keywords: Emulsification, Diesel, Bio-oil

1. INTRODUCTION

Bio-oil possesses the characteristics of both corrosiveness and lower heating values, and therefore it is not suitable as a fuel for direct usage. In order to improve the applicability of the bio-oil, improvements in its properties are to be made. By blending bio-oil with fossil fuel (e.x. diesel), several characteristic disadvantages as described above are diluted. Thus, bio-oil could be used in diesel combustion engines. Due to the difference in the dipole moment between bio-oil and diesel, bio-oil is immiscible with diesel and thus a heterogeneous mixture of bio-oil and diesel could be observed. When the heterogeneous mixture of bio-oil and diesel is put into a combustion chamber, numerous problems arise including: poor atomization, poor ignition, and incomplete combustion. These problems could be solved by using emulsification technology, which emulsifies the mixture of bio-oil and diesel into a homogeneous mixture. Chiaramontia et al[1,2]. studied emulsification of bio-oil/diesel mixtures with weight percentages of 25, 50 and 75% bio-oil and application status of emulsions in unmodified diesel engines. They found that emulsion under 70℃ could keep a homogeneous state for 3 days. The diesel engine that uses emulsions as fuel does not need a great amount of modification. Because of the corrosiveness of the emulsion, corrosion resistant material (e.x. stainless steel and ceramics) are recommended for nozzle and fuel pump components of a diesel engine. As the weight percentage of bio-oil increases, the viscosity of the emulsion increases. When concentration of an emulsifier is within the range of 0.5 to 2.0 wt%, the viscosity of the emulsion is suitable for a diesel engine. Some published writings[3,4] showed the methods for emulsification of various bio-oils in diesel: (1) First, by a method of trial-and-error, to obtain the optimal HLB (hydrophilic lipophilic balance) value of the emulsifier. (2) The bio-oils are then emulsified by using the emulsifier with the optimal HLB value. (3) Lastly, the emulsions are checked by the analysis of the emulsion properties to match the needs of the application. The trial-and-error method in finding an optimal HLB value of emulsifier is costly and time consuming. In this study, the relationship between bio-oils of different properties and optimal HLB values of the emulsifier is researched for developing an emulsification method of various bio-oils in diesel.

2. EXPERIMENTS

2.1 Determination of optimal HLB value of emulsifier

In this study, bio-oil was converted from waste wooden pallets and diesel purchased from CPC Corporation, Taiwan. Span 80 and Tween 80 were used as the base materials for preparation of the emulsifier. According to Eq.1 cited from Griffin[5,6], the HLB value of emulsifier can be calculated.

$$(HLB_1 \times w_1 + HLB_2 \times w_2 + \ldots) / (w_1 + w_2 + \ldots) = \text{HLB value of emulsifier} \cdots\cdots\cdots\cdots \quad (1)$$

In Eq.1, HLB_1 and HLB_2 are the HLB values of Span 80 and Tween 80 respectively, and w_1 and w_2 are the weight percentages of Span 80 and Tween 80 respectively. The procedure for determination of optimal HLB value of emulsifier is shown in Fig.1. Weight 19 g of diesel and 2 g of emulsifier, and allow the emulsifier to dissolve completely into diesel. Then drip the bio-oil into the mixture of diesel and emulsifier. After dripping each drop of bio-oil into the mixture, record the weight that was dripped and then homogenize the mixture of diesel, emulsifier, and bio-oil. Through vortex vibrator (Hipoint, mod. HM-300), homogenizing the mixture of diesel, emulsifier, and bio-oil to produce an emulsion. Visual measurement was used to determine if the emulsion was heterogeneous or not. With a significant difference in specific gravity between bio-oil and diesel (1.2 and 0.85, respectively), bio-oil deposits to the bottom upon mixing of bio-oil and diesel. With the assistance of a light source, the emulsion could be easily observed for any appearance of sediment. If any sediment was observed, then the emulsion was considered a heterogeneous emulsion. If the emulsion remained a homogeneous emulsion after a 15 min time interval, an emulsion stability condition is achieved. After reaching the emulsion stability condition, the dripping of bio-oil was continued until the stability condition could no longer be met. The procedure was repeated, changing the HLB values of the emulsifier, then the optimal HLB value of the emulsifier could be determined.

2.2 Emulsion production

The production procedure of the emulsion is shown in Fig.2. In this study, a steel barrel with a volume of 120 L equipped with a high speed homogenizer was used for the production of emulsion. The given amount of both emulsifier and diesel was weighed first, and then the emulsifier was mixed thoroughly with the diesel. A weighed amount of bio-oil was then blended into the mixture of emulsifier and diesel. The MICCRA D15 homogenizing device was used to homogenize the mixture of diesel, emulsifier, and bio-oil to produce an emulsion. Under homogenization, the emulsion is divided into a few samples. Each sample of the emulsion was homogenized with the following conditions: homogenization time (10 min) and homogenizer rotation speed (8800 to 16700 rpm). The rotation speed of the homogenizer was adjusted by the flow conditions of the diesel, bio-oil, and emulsifier mixture. After homogenization, sampling of the emulsion was done. Lastly, the samples sampled from the liquid surface and from the bottom of the emulsion were analyzed for their properties such as gross heating value, moisture and viscosity to check for the homogeneity of the emulsion.

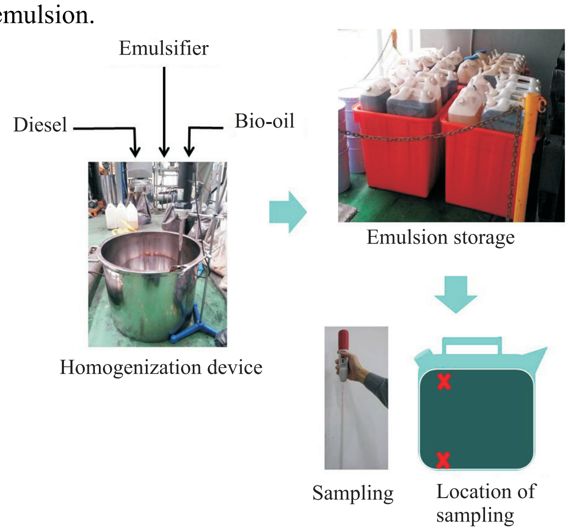

Fig.2. Procedure for emulsion production.

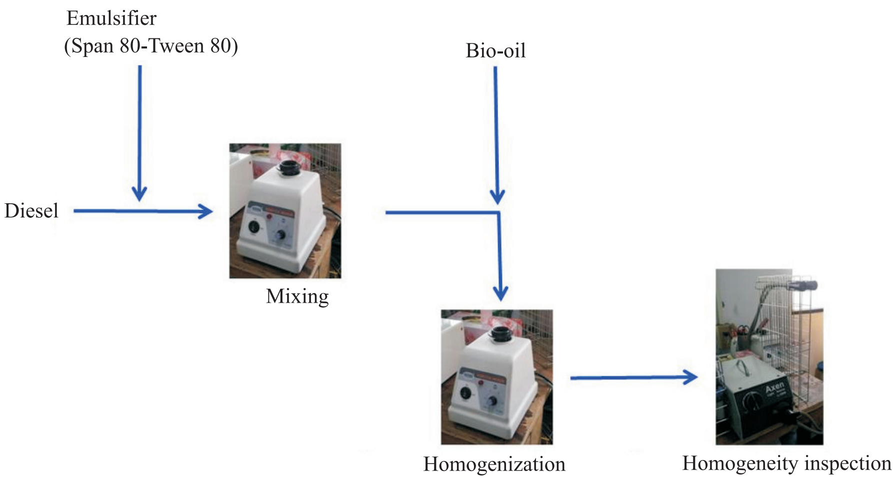

Fig.1. Procedure for the determination of the optimal HLB value of the emulsifier.

3. RESULTS AND DISCUSSIONS

The results of determining optimal HLB value of emulsifier for emulsifying various bio-oils in diesel are shown in Table 1 and Fig.3. Figure 4 shows the relationship between the gross heating values of the bio-oils and the optimal HLB values of the emulsifiers. As shown in Fig.4, the gross heating values of the bio-oils and the optimal HLB values of the emulsifiers show a linear relationship. As the gross heating value of the bio-oil increases from 2237 to 4836 cal/g, the optimal HLB value of the emulsifier decreases from 7.5 to 5.5. By regression analysis, the linear relationship could be expressed in Formula 2.

$$\text{(Optimal HLB value of emulsifier)} = -0.0008 \times \text{(Gross heating value of bio-oil)} + 9.2034 \quad (2)$$

This Formula 2 helps us to select an emulsifier in the emulsification of various bio-oils in diesel.

3.1 Concentration of emulsifier

It is helpful for setting up the composition of the emulsion to understand how the concentration of the emulsifier is affected by the concentration and the gross heating value of the bio-oil in the specific stability condition of the emulsion. In order to analyze the factors (concentration and gross heating value of bio-oil), some bio-oil/diesel emulsions are prepared with the emulsion stability of 15 min. The compositions of the emulsions are shown in Table 2 and Fig.5. Table 2 and Figure 5 showed that under specific conditions of emulsion stability, the concentration of the emulsifier increases along with the gross heating value or the concentration of the bio-oil. Using the concepts of liquid-liquid equilibrium diagram of fluid explains the results

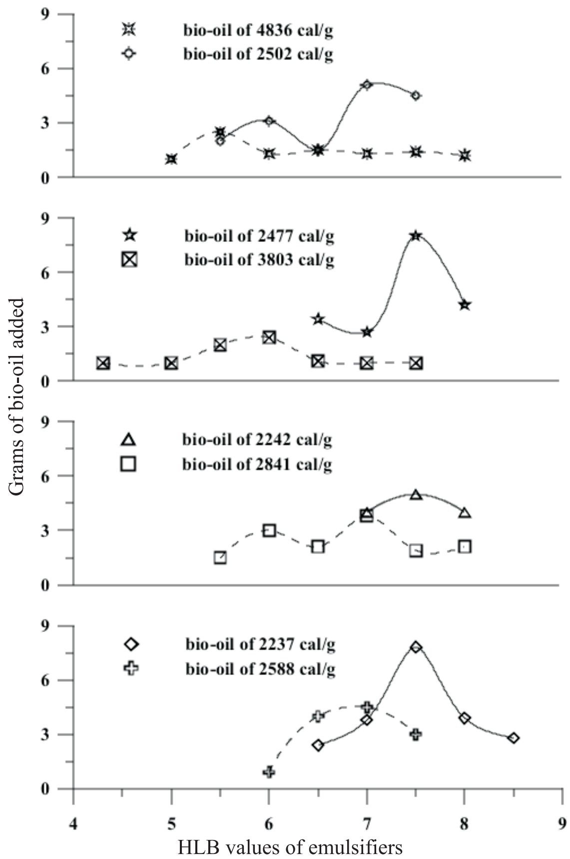

Fig.3. Results for determination of optimal HLB value of emulsifier.

Table 1 Results of determination of the optimal HLB value of the emulsifier

Number of bio-oil	1	2	3	4	5	6	7	8
Gross heating value of bio-oil (cal/g)	2237	2242	2477	2502	2588	2841	3803	4836
HLB value of emulsifier	Grams of bio-oil added							
4.3	-	-	-	-	-	-	1.0	-
5.0	-	-	-	-	-	-	1.0	1.0
5.5	-	-	-	2.0	-	1.5	2.0	2.5
6.0	-	-	-	3.1	0.9	3.0	2.4	1.3
6.5	2.4	-	3.4	1.5	4.0	2.1	1.1	1.5
7.0	3.8	4	2.7	5.1	4.5	3.8	1.0	1.3
7.5	7.8	5	8.0	4.5	3.0	1.9	1.0	1.4
8.0	3.9	4	4.2	-	-	2.1	-	1.2
8.5	2.8	-	-	-	--	-	-	-

Table 2 Bio-oil/diesel emulsions

Composition of bio-oil/diesel emulsion			Property of the used material		Composition of emulsifier	
Bio-oil (wt%)	Emulsifier (Span 80-Tween 80) (wt%)	Diesel (wt%)	Gross heating value of bio-oil (cal/g)	HLB value of emulsifier	Span 80 (wt%)	Tween 80 (wt%)
4.88	2.34	92.78	2237	7.5	70.10	29.90
27.08	6.94	65.97	2237	7.5	70.10	29.90
39.60	10.50	49.89	2237	7.5	70.10	29.90
3.42	2.48	94.11	2442	7.5	70.10	29.90
25.48	7.18	67.34	2442	7.5	70.10	29.90
6.02	2.46	91.52	2477	7.5	70.10	29.90
27.69	6.89	65.43	2477	7.5	70.10	29.90
32.49	7.78	59.74	2477	7.5	70.10	29.90
19.63	7.65	72.71	2502	7.0	74.77	25.23
4.08	2.74	93.19	2588	7.0	74.77	25.23
17.72	7.86	74.41	2588	7.0	74.77	25.23
15.30	8.60	76.10	2841	7.0	74.77	25.23
10.25	8.55	81.20	3803	6.0	84.00	16.00
2.64	2.54	94.81	4836	5.5	88.79	11.21
10.68	8.51	80.82	4836	5.5	88.79	11.21
14.82	14.94	70.24	4836	5.5	88.79	11.21

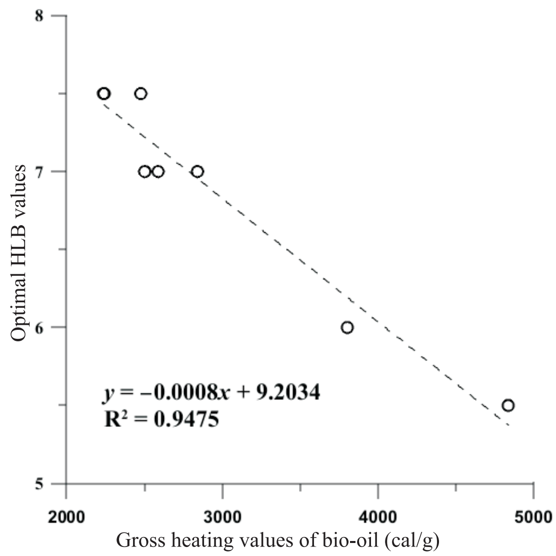

Fig.4. The relationship between the gross heating values of bio-oils and the optimal HLB values of the emulsifiers.

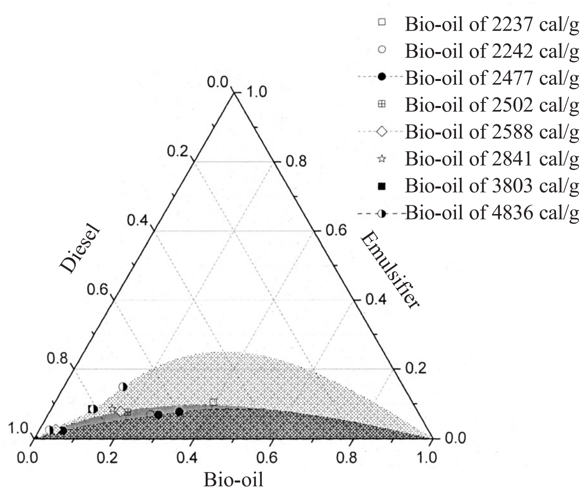

Fig.5. The compositions of the emulsions.

showed in Fig.5. If the composition of the emulsion is located in the homogeneous region of the mixture (blank region) the emulsion would be known as a homogeneous emulsion. Conversely if the emulsion is located in the heterogeneous region (shadow region) the emulsion would be known as a heterogeneous emulsion, where smaller areas of the heterogeneous region represent an emulsifier having a better emulsification capacity, due to the lower concentration of emulsion in the emulsion production.

3.2 Tracking of emulsion homogeneity

Since diesel does not contain water and the moisture in the bio-oil is around 21 to 58.5 wt%. When the bio-oil deposits in the bottom of the emulsion, the component in the liquid surface of emulsion should be pure diesel. Thus the sample sampled from the liquid surface of the emulsion could be analyzed for checking the homogeneity of the emulsion. If the moisture of the sample sampled from the liquid surface of the emulsion is close to zero, this means that the emulsion has become heterogeneous. This method of detecting homogeneity is used for large volumes of emulsion in the tracking of emulsion homogeneity. In this study, an emulsion of 100 liters was produced. The 100 liters of emulsion was prepared via the emulsification method developed in this study. The gross heating value of the bio-oil used in the preparation of the 100 liters of emulsion was 2491 cal/g. The optimal HLB value of emulsifier is 7.2, calculated from the formula of linear relationship. We used a special emulsifier which is called CSC-1 and its HLB value is 6. The concentration of bio-oil in the 100 liters of emulsion was set to 3 wt%. Referring to Table 2, the concentration of emulsifier should be higher than 2.48 wt%. Therefore, 3 wt% was used as the concentration of CSC-1. The homogeneity of the 100 liters of emulsion was tracked and the tracking results are shown in Fig.6. "UP sample" and "DN sample" represent the samples sampled from the liquid surface and bottom of the emulsion, respectively. Tracking results of gross heating values and viscosities of emulsion are also shown in Fig.6. Figure 6 illustrates the stability of the emulsion during the storage period of 33 days.

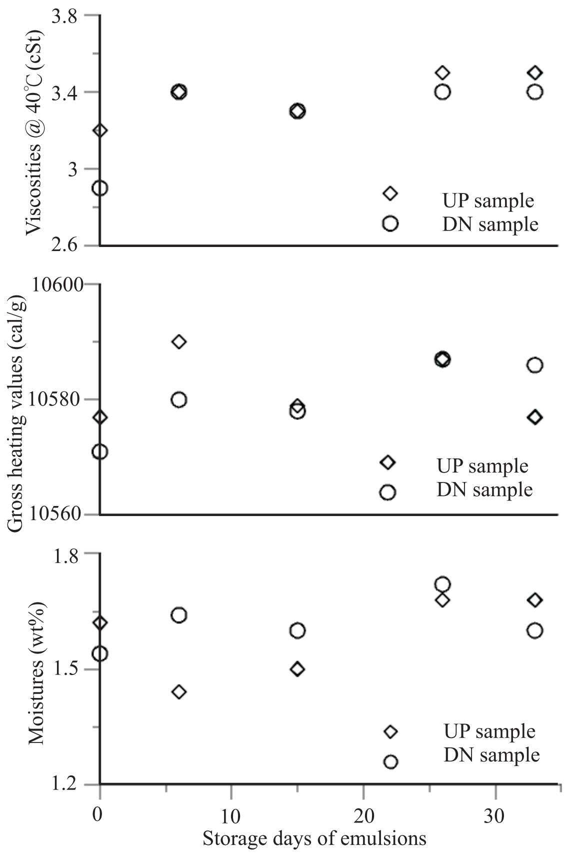

Fig.6. The tracking results for the homogeneity of the emulsion.

4. CONCLUSIONS

The present study develops a systematic method to emulsify a variety of bio-oils in diesel. A linear relationship between the gross heating values of bio-oils and the optimal HLB values of the emulsifiers was found in this work. The equation of the linear relationship is helpful for the determination of the optimal HLB value in the emulsification of a variety of bio-oils and diesel. The concentration of the emulsifier should be increased for emulsifying the bio-oil with a higher gross heating value, or for the mixture of bio-oil and diesel with higher concentrations of bio-oil. The track results of the homogeneity of emulsion showed the developed emulsification method in this study is feasible to produce stable emulsion for over 30 days.

REFERENCES

1. D. Chiaramonti, M. Bonini, E. Fratini, K. Gartner, A. V. Bridgwater, H. P. Grimm, I. Soldaini, A. Webster and P. Baglioni: "Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines-Part 1: emulsion production", Biomass Bioen., 2003, vol. 25, pp. 85-99.
2. D. Chiaramonti, M. Bonini, E. Fratini, K. Gartner, A. V. Bridgwater, H. P. Grimm, I. Soldaini, A. Webster and P. Baglioni: "Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines-Part 2: Tests in diesel engine", Biomass Bioen., 2003, vol. 25, pp. 101-111.
3. J. Y. Yu, Y. L. Peng, Y. F. Li, Z. Li, W. M. Yi and X. Y. Bai: "Stability of emulsion from bio-oil and diesel", Journal of Shandong University of Technology (Natural Science Edition), 2007, vol. 21, pp. 101-103.
4. Q. Wang, X. Li, S. Wang, Z. Luo and K. Cen: "Experimental research on emulsions from biomass pyrolysis liquid and diesel", Acta Energiae Solaris Sinica, vol. 31, pp. 380-384.
5. W. C. Griffin: "Classification of Surface-Active Agents by "HLB", Journal of the Society of Cosmetic Chemists, 1949, vol. 1, p. 311.
6. W. C. Griffin: "Calculation of HLB Values of Non-ionic Surfactants", Journal of the Society of Cosmetic Chemists, 1954, vol. 249, p. 5. □