



DET NORSKE VERITAS

Final Report
Setting Safe Limits on Biodiesel
Constituents for Pipeline Integrity

Pipeline & Hazardous Materials Safety Administration
U.S. Department of Transportation

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<p>Setting Safe Limits on Biodiesel Constituents for Pipeline Integrity</p> <p>For:</p> <p>Pipeline & Hazardous Materials Safety Administration U.S. Department of Transportation East Building, 2nd Floor 1200 New Jersey Ave., SE Washington, DC 20590</p> <p>Account Ref.:</p>	<p>DET NORSKE VERITAS (U.S.A.), INC. Materials & Corrosion Technology Center 5777 Frantz Road Dublin, OH 43017-1386, United States Tel: (614) 761-1214 Fax: (614) 761-1633 http://www.dnv.com http://www.dnvcolumbus.com</p>
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Executive Summary

Biodiesel (B100) is briefly defined as the monoalkyl esters of oils or fats. The demand for biodiesel and biodiesel blends as a fuel source has increased exponentially in the last decade. Today in the United States, nearly every Original Equipment Manufacturer (OEM) has approved the use of biodiesel blends of up to 5% (B5). According to the National Biodiesel Board (NBB), the yearly production of B100 has increased from approximately 0.5 million gallons in 1999 to 450 million in 2007. A current estimate indicates that nearly 170 biodiesel plants are operational in the U.S. as of 2008 with a projected production volume of 1.5 billion gallons (bg) by the end of 2009. In addition, new regulations will force a significant growth in biodiesel production during the next 5 years. The most recent Renewable Fuel Standards issued by the U.S. Environmental Protection Agency specifies a number of alternative biofuels, including corn-based ethanol, cellulosic ethanols, biodiesels, and other advanced biofuels that may be manufactured in the future using hitherto unknown technologies. The standard does not provide specific targets for biodiesel because the technology for its manufacture is still evolving. Significant research efforts are underway to manufacture biodiesel from algae. If successful, the biodiesel volumes could increase enormously, eclipsing other biofuels.

Pipeline transportation can save up to 20 cents a gallon of fuel transported over trucks and can result in other benefits such as lower greenhouse gas emissions and decreased hazards due to highway accidents. The benefits of pipeline transportation are predicated upon addressing all the integrity and operational issues.

Corrosion studies in biodiesel have not been conducted under pipeline specific conditions. The objectives of this work are to: (1) understand the effects of minor constituents beyond the ASTM D 6751 on corrosivity of biodiesel under pipeline specific conditions, (2) develop safe limits for any deleterious constituents in biodiesel, and (3) develop a method to rapidly measure biodiesel corrosivity in terms of any deleterious effect on pipeline integrity.

Because PHMSA decided to terminate the project much earlier than the originally planned ending date, the work scope and the objective were modified based on the feedback obtained during the kickoff meeting and the available financial resource.

The key results based on the adjusted work scope are:

1. A questionnaire was sent to various companies revealed the following aspects that may be important with respect to corrosion:
 - Biodiesel manufacturers regard water and glycerin as the most important impurities that could be present in biodiesel in the case of an upset;
 - Pipeline companies have been requested to transport a variety of biodiesel blends;



- A significant minority of responders indicated that they see a need for a corrosivity test and such a test is not currently available;
 - A number of impurities are anticipated, including rust particles, organic acids, and water;
 - Microbiologically influenced corrosion (MIC) was not a concern for many responders ;
 - Oxygen ingress is a concern for a majority of responders;
 - Internal coatings are seldom used, but drag reducing agents and other chemicals are added;
2. Biodiesel corrosivity evaluation suggested:
- Electrochemical Impedance Spectroscopy (EIS) is not a proper technique to obtain corrosion rate of carbon steel in biodiesel; Multiple Microelectrode Array (MMA) was demonstrated to be able to capture the corrosion current of the steel when exposed to the water phase of the biodiesel and water mixture;
 - Corrosion of carbon steel in biodiesel in the absence of added contaminants was minimal at most likely due to the high solution resistance of biodiesel;
 - Water phase in the biodiesel and water mixture could cause appreciable corrosion on carbon steel;



Table of Contents

1.0 BACKGROUND 1

2.0 PROJECT OBJECTIVE 3

3.0 RESULTS 4

 3.1 Task 1: Survey with Stakeholders on Biodiesel Related 4

 3.2 Task 2: Corrosivity Evaluation of Biodiesel..... 11

 3.2.1 Conductivity and Corrosivity of Biodiesel Measured by
 Electrochemical Impedance Spectroscopy (EIS)..... 12

 3.2.2 Carbon steel corrosion evaluation in biodiesel and water
 mixture using Multiple Microelectrode Array (MMA) 16

4.0 GENERAL DISCUSSION 19

5.0 SUMMARY 20

6.0 REFERENCES 21



List of Tables

Table 1. Questionnaire used in the survey with various stakeholders 4

Table 2. Summary of the survey results..... 8



List of Figures

Figure 1. The U.S. Renewable Fuel Standard issued by EPA [5].	1
Figure 2. EIS results obtained on a carbon steel wire (0.5 mm diameter) in SFGE	12
Figure 3. Schematic of the cell with two parallel electrodes for performing EIS in biodiesel	13
Figure 4. Two-electrode electrochemical cell for performing EIS using electrodes with 1 cm ² surface area.	13
Figure 5. Two-electrode cell for performing EIS using electrodes with 28 cm ² surface area.	14
Figure 6. A bode plot obtained in B5 solution using the two-electrode cell using electrodes with 1 cm ² surface area.	15
Figure 7. Comparison of the solution resistance obtained in EIS for petrodiesel (B0), biodiesel blends and E95.	15
Figure 8. Comparison of the corrosion rates converted from polarization resistance obtained in EIS for petrodiesel (B0), biodiesel blends and E95.	16
Figure 9. Current change as a function of time in the first day of the exposure.	17
Figure 10. Appearance of the electrode array after two weeks of exposure to the biodiesel and water mixture.	18
Figure 11. Comparison of the current on the electrodes in the electrode array during the exposure in the biodiesel and water mixture (current unit: A).	19

1.0 BACKGROUND

Biodiesel (B100) is briefly defined as the monoalkyl esters of oils or fats [1]. The demand for biodiesel and biodiesel blends as a fuel source has increased exponentially in the last decade. Today in the United States, nearly every Original Equipment Manufacturer (OEM) has approved the use of biodiesel blends of up to 5% (B5) [2]. According to the National Biodiesel Board (NBB), the yearly production of B100 has increased from approximately 0.5 million gallons in 1999 to 450 million in 2007 [3]. A current estimate indicates that nearly 170 biodiesel plants are operational in the U.S. as of 2008 with a projected production volume of 1.5 billion gallons (bg) by the end of 2009 [4]. In addition, new regulations will force a significant growth in biodiesel production during the next 5 years. The most recent Renewable Fuel Standards issued by the U.S. Environmental Protection Agency [5] specifies a number of alternative biofuels, including corn-based ethanol, cellulosic ethanols, biodiesels, and other advanced biofuels that may be manufactured in the future using hitherto unknown technologies (Figure 1). The standard does not provide specific targets for biodiesel because the technology for its manufacture is still evolving. Significant research efforts are underway to manufacture biodiesel from algae. If successful, the biodiesel volumes could increase enormously, eclipsing other biofuels.

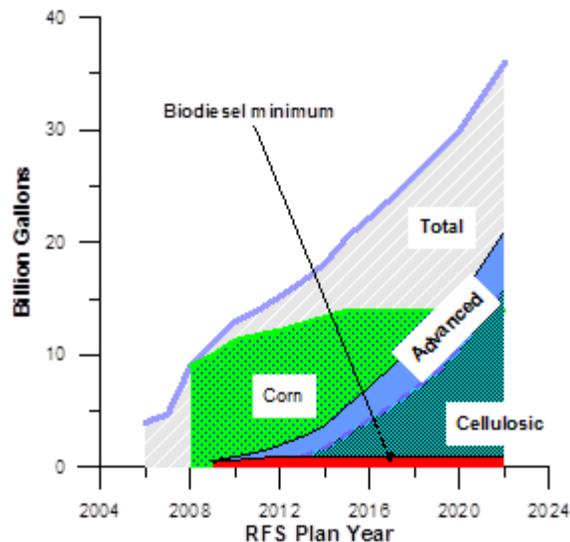


Figure 1. The U.S. Renewable Fuel Standard issued by EPA [5].

Pipeline transportation can save up to 20 cents a gallon of fuel transported over trucks and can result in other benefits such as lower greenhouse gas emissions and decreased hazards due to highway accidents. The benefits of pipeline transportation are predicated upon addressing all the integrity and operational issues.

Corrosion studies in biodiesel have not been conducted under pipeline specific conditions. The Steel Tank Institute [6] conducted a study of corrosion of steel in two different biodiesels mixed in varying proportions with ultra-low sulfur diesel with and without small water additions within the ASTM specification. The corrosion rates in both biodiesels and their blends were quite low based on a 2-month mass-loss measurement. Lee et al. [7] examined the microbiological activity and corrosion in soy-based biodiesel mixed with ultra-low sulfur diesel and water. Because of the 50-50 diesel-water mixtures, they were able to perform electrochemical measurements only in the water layer. The influence of biodiesel was found to be insignificant or even beneficial in terms of microbiologically influenced corrosion. In both these cases, tests were conducted under static conditions that would be expected in tanks and fuel storage systems. In pipelines, corrosion under flowing conditions is important. Kane and Papavinasam [8] identified a number of knowledge gaps in corrosion of biodiesel including limitation of the copper strip corrosivity measurement, lack of quantitative knowledge of corrosivity of various biodiesels especially when they are commingled, and lack of correlation between biofuel chemistry and corrosivity.

B100 chemistry specification is contained in ASTM D6751-09 and it has been approved as a component in conventional diesel fuels at 5, 6, and 20 volume percent (B5, B6, and B20). A number of new biodiesel sources are anticipated in the future, such as from algae processing. These biodiesels will have to meet ASTM D 6751, but may contain other constituents not listed in ASTM specifications. The only corrosion-related requirement in ASTM D6751 is the copper strip test (ASTM D130). The copper strip corrosivity test (ASTM D130) is a particularly poor test because it is qualitative, subjective, and it has no relevance to materials and conditions in pipelines. Therefore, a pipeline-relevant corrosion test is necessary to establish the effects of potentially deleterious constituents in biodiesel under pipeline conditions. Secondly, even if the deleterious constituents are identified, it will be necessary to establish a rapid monitoring method to identify potentially harmful biodiesels prior to introducing them in pipelines.

Three pipeline corrosion scenarios can be identified: (1) corrosion directly from biodiesel or its blends; (2) corrosion from any residual water phase (e.g., water left accidentally by prior hydrotesting) that is overlain by a biodiesel layer whose chemistry affects the corrosivity of the water phase through diffusion of chemical species from biodiesel phase; and (3) corrosion by an emulsion of water and biodiesel or its blend. The harmful effect of biodiesel is unlikely to be directly from Scenario 1 since most tests to date have indicated the corrosivity of biodiesel to be relatively low, but Scenarios 2 and 3 may lead to higher corrosion. However, the effect of different constituents in various biofuels on corrosion is not known. There is a need to develop knowledge of which constituents in biodiesel could adversely affect corrosion, either singly or in combination, and what limits should be set to minimize internal corrosion problems.

2.0 PROJECT OBJECTIVE

The objectives of this work are to: (1) understand the effects of minor constituents beyond the ASTM D 6751 on corrosivity of biodiesel under pipeline specific conditions, (2) develop safe limits for any deleterious constituents in biodiesel, and (3) develop a method to rapidly measure biodiesel corrosivity in terms of any deleterious effect on pipeline integrity.

A kickoff meeting was held on December 3, 2010 with various stakeholders to discuss the project objectives and proposed tasks. The web-based kickoff meeting was attended by a representative from the National Biodiesel Board, representatives from several pipeline companies, PHMSA staff, a representative from Pipeline Research Council International (PRCI), and a representative from the Steel Tank Institute (STI). The project team presented the objectives of the project, the different tasks, discussed the need to plan a matrix of tests and emphasized the need to obtain diesel samples for the testing.

As the first outcome of this kickoff meeting, a survey questionnaire was prepared to send to various stakeholders and obtain feedback. This feedback will be used to determine the test matrix. Other recommendations made as a result of this meeting include:

1. Conduct a preliminary investigation of the range of corrosion rates to be expected in biodiesel samples as a result of the variation of biodiesel chemistry itself, rather than other impurities present
2. Determine whether the project should come up with a corrosivity performance specification (and a test method) rather than an impurity limit specification
3. Perform tests in a baseline diesel for comparison

The group felt that sending out a survey to various stakeholders and obtaining a range of biodiesel samples will be an important first step.

Additionally, PHMSA decided to terminate the project much earlier than the originally planned ending date. Therefore, the work scope and the objective were modified based on the feedback obtained during the kickoff meeting and the available financial resource. The following tasks were accomplished:

Task 1: Survey with Stakeholders on Biodiesel Related Issues

Task 2: Evaluation of Corrosion Test Methods



3.0 RESULTS

3.1 Task 1: Survey with Stakeholders on Biodiesel Related

The survey is grouped into the following categories:

- Manufacturing related factors
- Factors involved in acceptance for pipeline transportation
- Factors during transportation
- Other factors

While the survey focuses mostly on corrosion of steel, feedback on other non-ferrous metals used in pipelines is also of interest. Other transportability issues, such as freezing, etc. are not of concern for this survey. The questionnaire is shown in Table 1.

Table 1. Questionnaire used in the survey with various stakeholders

Contact information for follow-up questions	Item	Comment
	Manufacturing Related Factors	
	M.1) Feedstock for biodiesel (i.e.: soy, canola, animal fats, etc)	
	M.1a) alcohol used (i.e. methanol, ethanol, etc.)	
	M.1b) catalyst used (i.e. sodium hydroxide, potassium hydroxide)	
	M.2) Type of process	
	M.3) Additives prior to sending it to pipelines (e.g., any stabilizing agents, biocides, inhibitors, etc.)	
	M.4) If upset conditions occur in process, what types of chemical species could enter into product? What would be the range of expected concentrations? (i.e., precursors, catalysts, glycerin, water, solids, etc.)	
	M.5) Storage method prior	

Contact information for follow-up questions	Item	Comment
	to pipelines (aboveground storage tanks, below ground storage tanks, salt caverns, etc.)	
	M.6) What blends will be supplied to pipelines? (BXX)	
	M.6a) What is the blending diesel source (petrodiesel, synthetic diesel, type and source)	
	M 7). Do you have chemical analysis from the above conditions? Would you be able to share?	
	Pipeline Acceptance Factors	
	A.1) Have you been approached by manufacturers for transporting biodiesel?	
	A.2) What type of blends have you considered transporting?	
	A.3) What is your current acceptance/risk assessment practice for biodiesel?	
	A.4) What type of analysis/test methods do you use for acceptance?	
	A.5) Other considerations for acceptance?	
	A.6) Do you see a need for other acceptance testing (i.e. corrosivity, physical or chemical tests)	
	A.6a) Do you have knowledge of relevant testing already available	

Contact information for follow-up questions	Item	Comment
	(i.e. NACE, ASTM, etc.)	
	Pipeline Transportation	
	What type of impurities (including water) do you expect to accumulate during transportation?	
	Have you experienced MIC due to bio or petrodiesel?	
	Are you concerned about MIC or corrosivity of biodiesel?	
	Is batching of biodiesel with other commodities likely on your pipeline system (or will biodiesel exist in tanks that also support other products?)	
	Do you have concerns about oxygen ingress?	
	Do you add any inhibitors or DRA?	
	What temperature ranges do you anticipate?	
	Is transmix a significant concern? If so, what concerns do you have?	
	Is unplanned shut-in a concern?	
	Other Issues	
	Other than steel, are there concerns with other metals with respect to biodiesel?	
	Do you have any internal coatings?	
	What other corrosion-related specification issue do you wish to address?	

The questionnaire was sent to various companies. By the time this report is written, however, only four companies responded to the questionnaire. Nevertheless, the following aspects that may be important with respect to corrosion were observed:

- Biodiesel manufacturers regard water and glycerin as the most important impurities that could be present in biodiesel in the case of an upset
- Pipeline companies have been requested to transport a variety of biodiesel blends
- A significant minority of responders indicated that they see a need for a corrosivity test and such a test is not currently available
- A number of impurities are anticipated, including rust particles, organic acids, and water
- Microbiologically influenced corrosion (MIC) was not a concern for many responders
- Oxygen ingress is a concern for a majority of responders
- Internal coatings are seldom used, but drag reducing agents and other chemicals are added

The detailed survey results are summarized below in Table 2.

**Table 2. Summary of the survey results.**

Category	Item #	Question	Comment	Percentage (%)
Manufacturing Related Factors	M.1a	Feedstock for biodiesel	Animal fat	28.6
			Waste cooking oil	28.6
			Canola	28.6
			Camolina	14.2
	M.1b	Alcohol used	Methanol	100.0
	M.1c	Catalyst used	Sodium methoxide	25.0
			Potassium hydroxide	25.0
			Sulfuric acid	25.0
			Potassium	25.0
	M.2	Type of process	Transesterification	33.3
			Batch/drywash	33.3
			Acid esterification, transesterification, distillation	33.3
	M.3	Additives prior to sending it to pipelines	None	33.3
			Antioxidant (Eastman BioExtend 30 solutions)	33.3
			Oxidative stability additive	33.3
	M.4a	If upset conditions occur in process, what types of chemical species could enter into product?	Glycerin	28.5
			Water	28.5
			Monoglycerides	14.3
			Drywash (magnesol)	14.3
			Not released for sale	14.3
	M.4b	What would be the range of expected concentrations of chemical species identified in M.4a?	Glycerin < %	28.5
			Water < 1000 ppm	14.3
			Water < 1%	14.3
Monoglycerides < 0.6%			14.3	
Drywash (magnesol) < 1%			14.3	
N/A			14.3	
M.5	Storage method prior	Above ground	100.0	



Category	Item #	Question	Comment	Percentage (%)
		to pipelines		
	M.6a	What blends will be supplied to pipelines? (BXX)	B100	33.3
			B99	33.3
			B2-B10	33.3
	M.6b	What is the blending diesel source?	Petrodiesel	100.0
	M.7	Do you have chemical analysis from the above conditions and would you be able to share?	No (conditions not encountered)	33.3
			Yes	66.6
Pipeline Acceptance Factors	A.1	Have you been approached by manufacturers for transporting biodiesel?	Yes (only by truck and rail)	33.3
			We are the manufacturer	33.3
			No	33.3
	A.2	What type of blends have you considered transporting?	N/A (only transport B100)	25.0
			B100	25.0
			B99.9	25.0
			B2-B5	25.0
	A.3	What is your current acceptance/risk assessment practice for biodiesel?	N/A	33.3
			BQ-9000 practices	33.3
			ASTM D6751	33.3
	A.4	What type of analysis/test methods do you use for acceptance?	N/A	33.3
			ASTM D6751	66.6
	A.5	Other considerations for acceptance?	N/A	66.6
			No	33.3
	A.6a	Do you see a need for other acceptance testing?	No	66.6
			Corrosivity	33.3
	A.6b	Do you have knowledge of relevant testing already available?	No	25.0
			ASTM	25.0
			EN	25.0
			Yes	25.0



Category	Item #	Question	Comment	Percentage (%)
Pipeline Transport	T.1	What type of impurities (including water) do you expect to accumulate during transportation?	Water (for transport by truck, rail, and 3 rd party storage)	16.7
			Rust flakes (for transport by truck, rail, and 3 rd party storage)	16.7
			Coarse organic residues (for transport by truck, rail, and 3 rd party storage)	16.7
			Water	16.7
			Organic acids	16.7
			Not sure	16.7
	T.2	Have you experienced MIC due to bio or petrodiesel?	No	100.0
	T.3	Are you concerned about MIC or corrosivity of biodiesel?	No	33.3
			Yes	33.3
			Not sure	33.3
	T.4	Is batching of biodiesel with other commodities likely on your pipeline system (or will biodiesel exist in tanks that also support other products)?	N/A	33.3
			Transport biodiesel only	33.3
			No	33.3
	T.5	Do you have concerns about oxygen ingress?	No	33.3
			Yes	66.6
	T.6	Do you add any inhibitors or DRA?	N/A	33.3
			Yes	66.6
T.7	What temperature ranges do you anticipate?	N/A (for tanks, B100 stored between 15°C and 60°C)	33.3	



Category	Item #	Question	Comment	Percentage (%)
			-15 to +35°C	33.3
			4.4 to 37.8°C	33.3
	T.8a	Is transmix a significant concern and if so, what concerns do you have?	N/A	33.3
			No	33.3
			Not with petroleum diesel	33.3
	T.9	Is unplanned shut-in a concern?	N/A	50.0
			Not sure	50.0
Other Issues	O.1	Other than steel, are there concerns with other metals with respect to biodiesel?	Brass	37.5
			Copper	37.5
			Aluminum	12.5
			Soft alloys	12.5
	O.2	Do you have any internal coatings?	No	100.0
	O.3	What other corrosion-related specification issue do you wish to address?	None	66.6
			Gaskets, hoses and other connections	33.3

3.2 Task 2: Corrosivity Evaluation of Biodiesel

Corrosion rate measurement by electrochemical technique in environments such as biodiesel is a great challenge due to the poor conductivity of the solution. It was demonstrated that the employment of small size electrode made it possible to perform electrochemical measurements in simulated grade fuel ethanol (SFGE) [9]. However, the initial attempt in using the same technique did not generate meaningful results for carbon steel in biodiesel. Thus, efforts were taken to measure the conductivity of biodiesel and its blends. The results were compared to that of SFGE to understand whether it is possible at all to perform electrochemical measurement in biodiesel. Efforts were also made to explore the possibility of using techniques that are frequently in less conductive aqueous environments to measure corrosion rate of steel in biodiesel. This section summarizes the obtained results from these efforts.

Two types of biodiesel were supplied by a pipeline operator: one based on fresh vegetable oil and the other based on used vegetable oil. The biodiesel from fresh vegetable oil was used in this work. Petrodiesel was used to blend with the biodiesel to get B5 and B20 blends (by volume).

3.2.1 Conductivity and Corrosivity of Biodiesel Measured by Electrochemical Impedance Spectroscopy (EIS)

Although EIS has been frequently used in corrosion investigation in less conductive aqueous media, it showed some artifacts when used in organic solvents that have poor conductivity. One example is shown in Figure 2 for a 0.5 mm carbon steel wire in SFGE. As seen, capacitance behavior was observed at frequency higher than 2 kHz, an artifact associated with the instrument and the cell geometry. Others have also observed such artifact in other systems [10, 11].

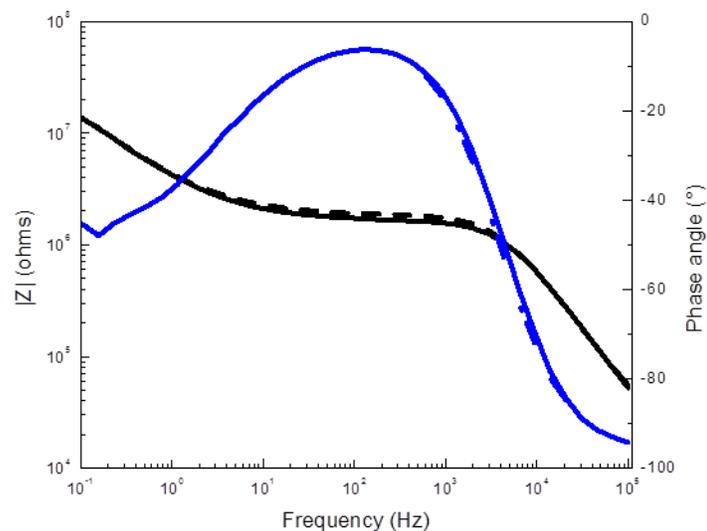


Figure 2. EIS results obtained on a carbon steel wire (0.5 mm diameter) in SFGE

In order to remove the artifact in high frequency region, a cell with two parallel electrodes was used. This testing configuration has been shown to improve the EIS results in ethanol by Souza and coworkers [11]. The two-electrode cell is shown in Figure 3 through Figure 5. Electrodes with two different surface areas (1 cm^2 and 2.78 cm^2) were used. The larger surface area would reduce the resistance between the two electrodes further.

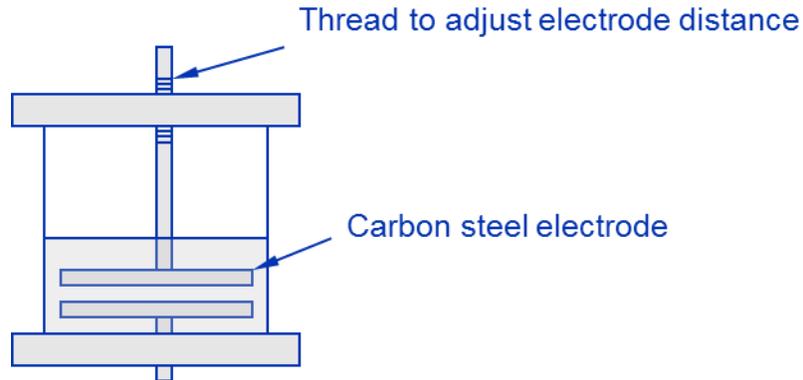


Figure 3. Schematic of the cell with two parallel electrodes for performing EIS in biodiesel

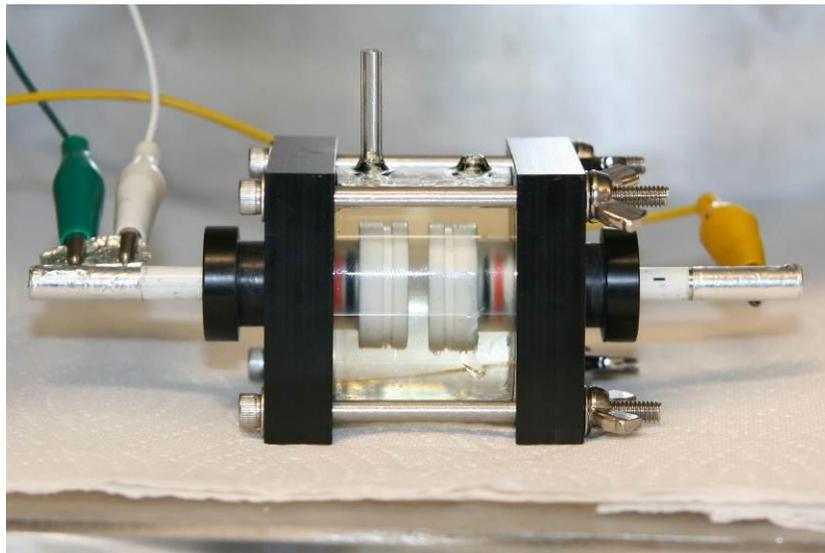


Figure 4. Two-electrode electrochemical cell for performing EIS using electrodes with 1 cm² surface area.

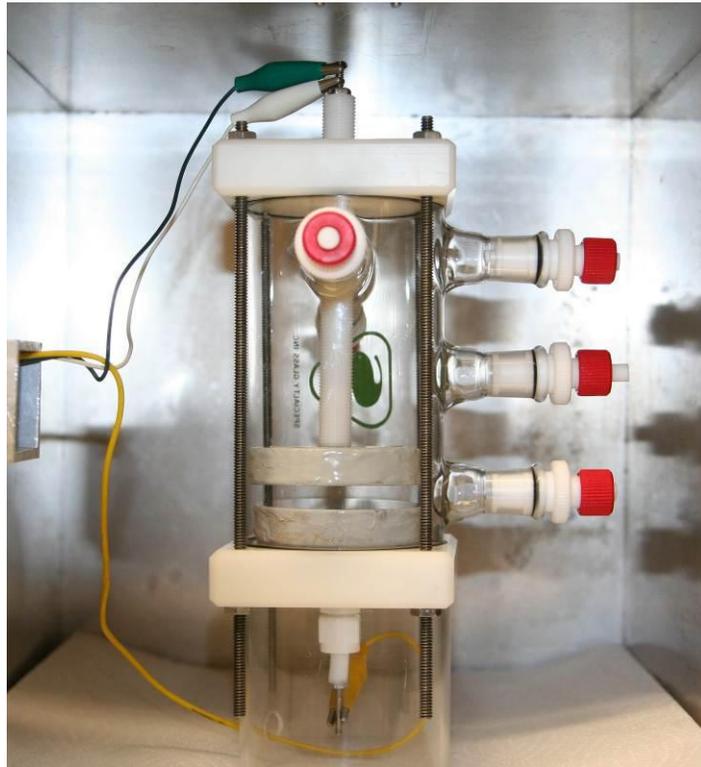


Figure 5. Two-electrode cell for performing EIS using electrodes with 28 cm² surface area.

Although the artifact observed in the EIS results were reduced using the electrochemical cell with two parallel electrodes, it is still challenging to obtain accurate corrosion rate using EIS in biodiesel. This is because the biodiesel is a very resistive media and thus large solution resistance at high frequencies as well as low frequency impedance, which is a combination of solution resistance and charge transfer resistance, was obtained, as shown in Figure 6. Subtracting two these numbers with large values to obtain charge transfer resistance (and thus corrosion rate) would lead to substantial error in the results.

The solution resistances for the petrodiesel and different biodiesel blends were compared to that of E95 in Figure 7. As can be seen, the solution resistances for the petrodiesel and biodiesel blends are substantially higher than that of E95. This would suggest the corrosion rate of carbon steel in petrodiesel and biodiesel blends should be considerably lower than in E95. This was confirmed by converting the polarization resistance obtained in EIS for carbon steel to corrosion rate for the tested solutions (Figure 8). Therefore, the corrosion caused by the diesel solution in the absence of any contaminants does not appear to be significant based on the limited number of tests performed in this project. The corrosion rates based on weight loss measurement in another PHMSA funded project (#WP382: Corrosion and Integrity Management of Biodiesel Pipelines) are similar to what was obtained in this project.

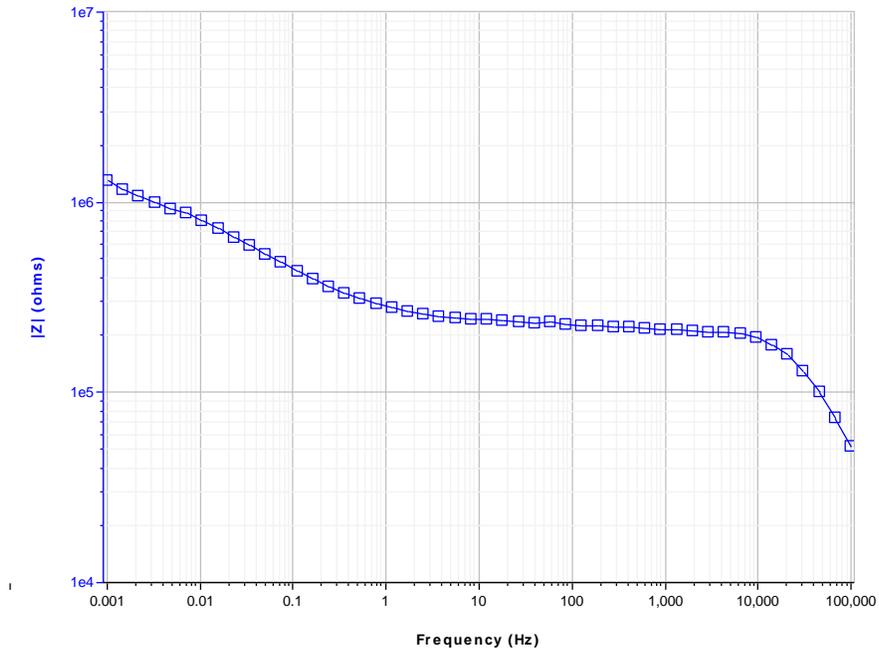


Figure 6. A bode plot obtained in B5 solution using the two-electrode cell using electrodes with 1 cm² surface area.

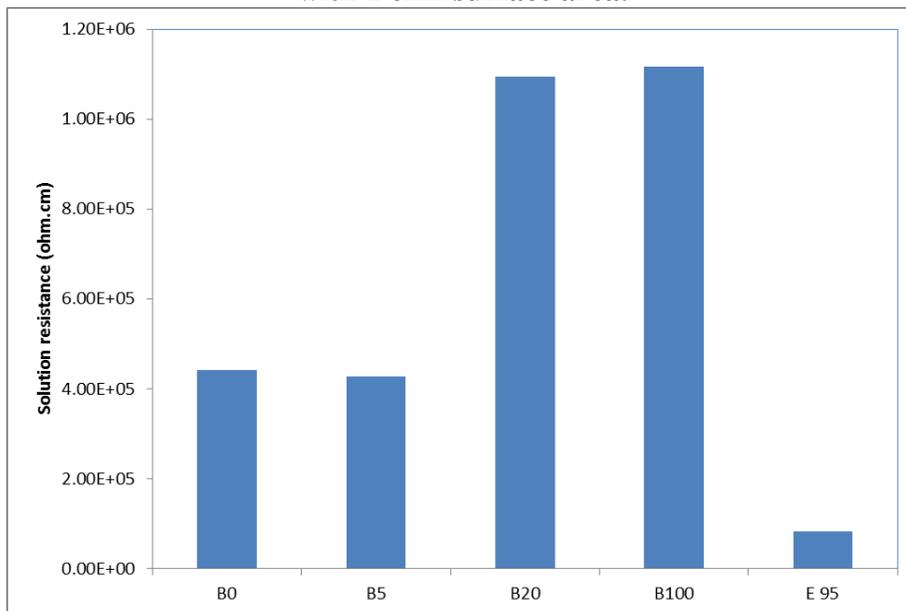


Figure 7. Comparison of the solution resistance obtained in EIS for petrodiesel (B0), biodiesel blends and E95.

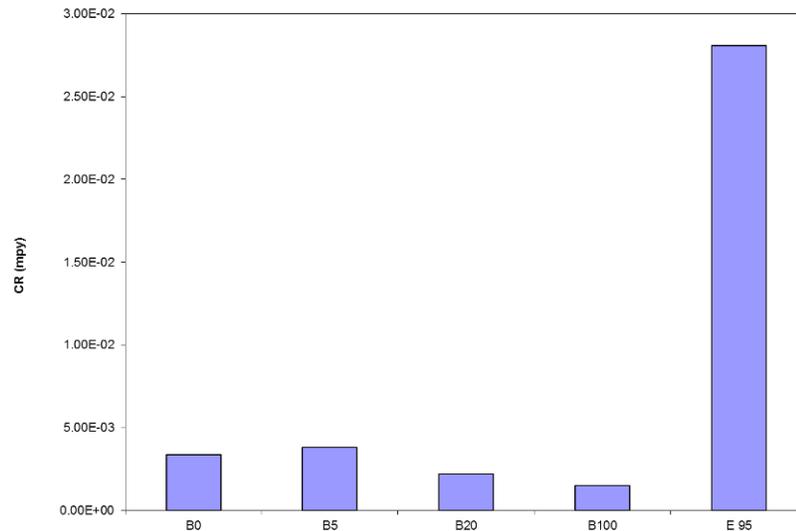


Figure 8. Comparison of the corrosion rates converted from polarization resistance obtained in EIS for petrodiesel (B0), biodiesel blends and E95.

3.2.2 Carbon steel corrosion evaluation in biodiesel and water mixture using Multiple Microelectrode Array (MMA)

As discussed above, biodiesel solution without any intentionally added contaminants would not cause significant corrosion of carbon steel. Thus, any corrosion that may be of concern would only be due to the contaminants. Because biodiesel is not miscible with water and phase separation could easily occur, it is possible pocket of water could exist in biodiesel storage facilities or dead legs in pipelines. The corrosion of carbon steel in such situation was investigated using a Multiple Microelectrode Array (MMA).

A MMA consists of any number of electrodes closely packed together to mimic a bulk metallic material. The electrodes are typically small so that the reactions on the electrodes are either anodic or cathodic ones. The MMA is connected to an MMA analyzer in which the current passed between the electrodes in the array could be measured using a zero resistance ammeter (ZRA). This technique allows the measurement of the corrosion current between anodic and cathodic sites in the array even at the corrosion potential. The ability of measuring corrosion current at corrosion potential in the case of biodiesel is particularly important since proper polarization on the sample is difficult due to the potential drop resulting from the high solution resistance.

In this work, the electrode array consists of 100 carbon steel 1018 wires (0.5 mm in diameter). These wires were packed closely in epoxy as a 5x20 matrix. The array then was exposed to a

mixture of biodiesel and deionized water (1:1 in volume). The electrode array was positioned in the cell such that the first six rows of the array were exposed to the top biodiesel phase whereas the rest of the array was exposed to the water phase. The electrode array was then connected to a MMA analyzer (Scribner MMA 900) and the current was monitored for two weeks.

The current change in the first day is shown in Figure 9. As shown, anodic sites developed (positive current) shortly after the test began. Integrating the anodic current could generate the charge passed during the corrosion process and thus make it possible to generate the corrosion rates. The electrodes exposed to the water phase were corroded appreciably after two weeks of exposure, as shown in Figure 10. No corrosion was seen on the electrodes exposed to the biodiesel phase, consistent with the observation in the EIS measurement discussed previously.

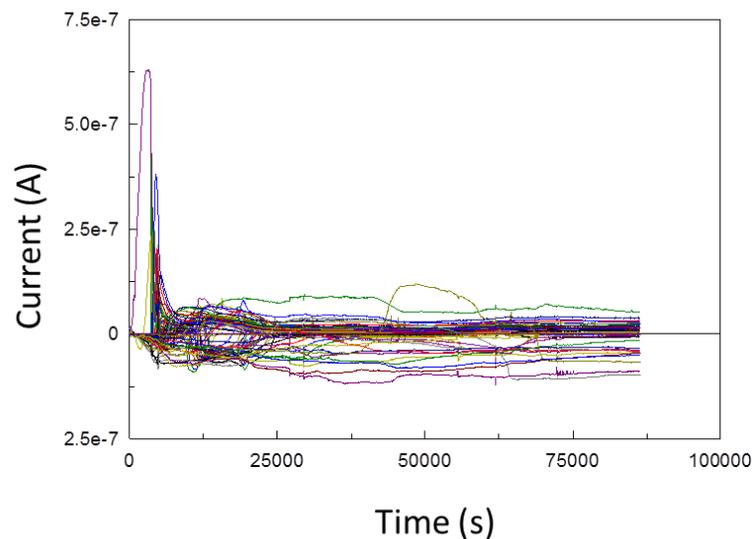
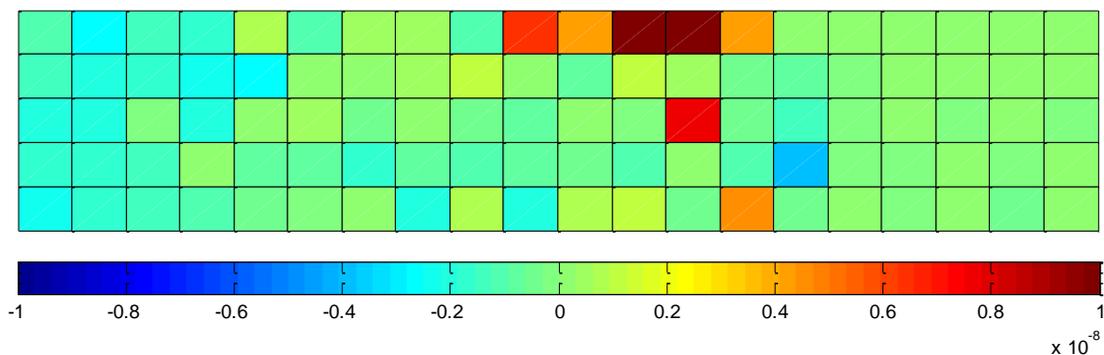


Figure 9. Current change as a function of time in the first day of the exposure.

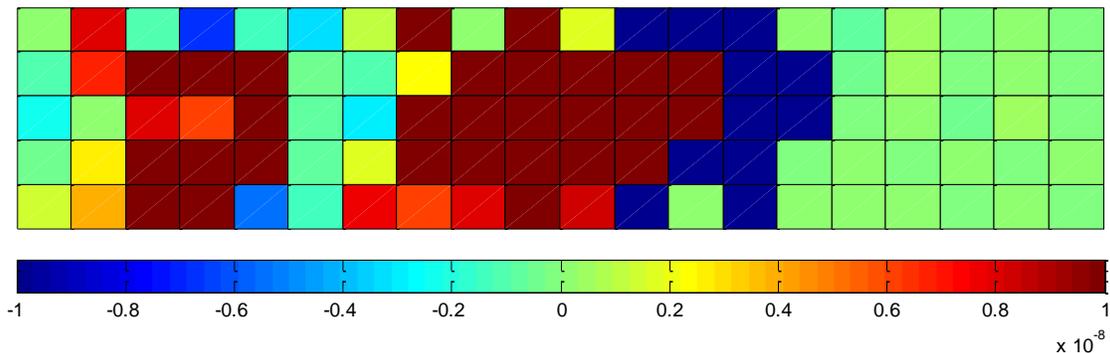


Figure 10. Appearance of the electrode array after two weeks of exposure to the biodiesel and water mixture.

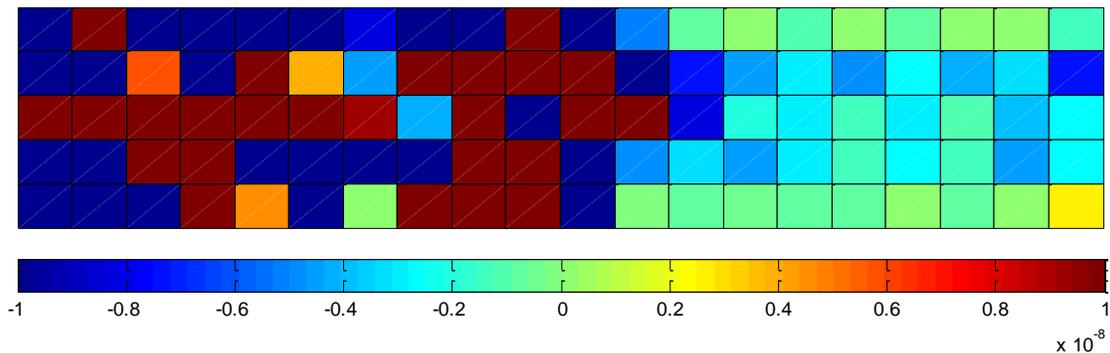
MMA also allows capturing the propagation of the corrosion sites during the exposure. As shown in Figure 11, the anodic sites (with current larger than 1×10^{-8} A) started on a few electrodes closed to the biodiesel-water interface. With increasing exposure time, the anodic sites propagated to locations farther away from the interface. This could suggest that the corrosion was a result of certain species diffusing from the biodiesel phase into the water phase. Further water chemistry analysis would be able to provide more information on the cause of the corrosivity change in the water phase.



(a). Corrosion current map showing corrosion initiation shortly after exposure



(b) Corrosion current after 1 day



(c) Corrosion current after two weeks

Figure 11. Comparison of the current on the electrodes in the electrode array during the exposure in the biodiesel and water mixture (current unit: A).

4.0 GENERAL DISCUSSION

The survey results suggested water is the most possible contaminant in biodiesel based on the limited number of response. In the subsequent corrosivity evaluation, it was observed that biodiesel does not impart substantial corrosion to carbon steel in the absence of any added contaminants, likely due to the high solution resistance that makes the corrosion processes difficult to occur. The corrosion rate of carbon steel in biodiesel blends was minimal at most and substantially smaller than in E95 in which general corrosion of carbon steel has been observed.

Because the survey indicated the importance of water with respect to the corrosion of carbon steel in biodiesel, the corrosivity of water phase mixed with biodiesel was investigated with MMA. MMA was demonstrated to be a useful technique in evaluating the corrosion of carbon steel in biodiesel and water mixture. Corrosion was seen in the water phase of the biodiesel and

water mixture. The corrosivity of the water phase was likely due to certain species (such as chloride) diffusing from the biodiesel phase into the water phase. It is unclear what species was responsible for the corrosion in the water phase without further analytical work on the water phase. Also, future studies should address the corrosivity of the water phase when present with biodiesel for different types of biodiesels with and without other contaminants (e.g., organic acids).

5.0 SUMMARY

A questionnaire sent to various companies revealed the following aspects that may be important with respect to corrosion:

- Biodiesel manufacturers regard water and glycerin as the most important impurities that could be present in biodiesel in the case of an upset;
- Pipeline companies have been requested to transport a variety of biodiesel blends;
- A significant minority of responders indicated that they see a need for a corrosivity test and such a test is not currently available;
- A number of impurities are anticipated, including rust particles, organic acids, and water;
- Microbiologically influenced corrosion (MIC) was not a concern for many responders ;
- Oxygen ingress is a concern for a majority of responders;
- Internal coatings are seldom used, but drag reducing agents and other chemicals are added;

Biodiesel corrosivity evaluation suggested:

- EIS is not a proper technique to obtain corrosion rate of carbon steel in biodiesel; MMA was demonstrated to be able to capture the corrosion current of the steel when exposed to the water phase of the biodiesel and water mixture;
- Corrosion of carbon steel in biodiesel in the absence of added contaminants was minimal at most likely due to the high solution resistance of biodiesel;
- Water phase in the biodiesel and water mixture could cause appreciable corrosion on carbon steel;

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