

Tracking Interfacial Adsorption/Desorption Phenomena in Polypropylene/Biofuel Media using Trace Cr³⁺/Cr⁶⁺ and As³⁺/As⁵⁺-A Study by Liquid Chromatography-plasma Mass Spectrometry

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Abstract

The effect of adsorption/desorption of biofuels on polymers cannot be directly measured unless the fuel is infused with a marker or tracer to track the impact of the phenomenon. Certain trace chemical species in biodiesel can serve as natural markers and our study investigated the use of such natural markers in neem biodiesel to indirectly evaluate the kinetics of adsorption and desorption. Chemical species Cr³⁺/Cr⁶⁺ and As³⁺/As⁵⁺ naturally present in biodiesel were employed as tracers to measure the rates of adsorption and desorption in polypropylene material following immersion in biofuel media for selected intervals. Ultra-sensitive hyphenated HPLC linked to ICP-MS was deployed to monitor these effects. Elution followed by mass spectrometry for simultaneous detection was conducted for convenient resolution of all four species. A C-8 reinforced silica column formed the stationary phase (150 mm in length; internal diameter: 4.6 mm; particle size: 5.0 μm). The mobile phase was a special mixture prepared by following a specific protocol. The elution rate was ~1.2 mL/min; and associated retention times (min) were: As³⁺: 1.61; As⁵⁺: 4.06; Cr³⁺: 3.71; and Cr⁶⁺: 5.80. The system is equipped with a dynamic reaction cell (DRC) to facilitate mass detection. The oxygen flow in the DRC was controlled to give a rate of ~0.4 mL/min. Following mass detection m/z values of 52 characterized the Cr³⁺/Cr⁶⁺ species; while the arsenic components were detected as adduct ions, AsO⁺, m/z 91, in association with oxygen. Certified reference materials were used to standardise the instrument. The results showed that the phenomenon is influenced by ionic charge and polarity of the medium. Water contamination of the biodiesel tends to augment the adsorption rate. The rates of adsorption/desorption based on the species of interest follow first order kinetics. Pronounced adsorption rate constants were observed in water infected biodiesel, between 0.3-0.5 wk⁻¹ for Cr⁶⁺ and As⁵⁺. The rate constants in "water free" samples dropped to about 0.1 wk⁻¹ for all species. The impact of our study is discussed in terms of the attrition that biofuels can have on polymeric materials.

Keywords: Polypropylene; Cr³⁺/Cr⁶⁺ and As³⁺/As⁵⁺; HPLC/ICP-MS; Neem biodiesel; Kinetics

Introduction

The abrasive effects of biofuels on rubber hosing and polymer fittings in vehicles and machinery are well known [1-3]. There is, therefore, a need for information on the kinetics of these effects for purposes of extending the durability of such materials. However, such effects of biofuels on polymeric material have not been previously reported and represent an underexplored area of study. It is known that biodiesel causes chronic attrition of polymers in vehicles and machinery [3-6] and adsorption/desorption kinetics could contribute to a deeper understanding of the phenomenon [8-12]. Monitoring kinetics of adsorption and desorption on polypropylene in neem biodiesel was the subject of our study undertaken specifically to obtain a broader knowledge of the general effects of biofuel on polymeric material.

Tracking adsorption/desorption effects in polymers is a challenge for the simple reason that no contemporary measurable technique exists for such tracking studies – unless the biodiesel itself contains natural "tracers" or "markers" to make this possible. We developed a unique method to evaluate the rates of adsorption and desorption by utilizing natural trace chemical species Cr³⁺/Cr⁶⁺ and As³⁺/As⁵⁺ present in the biodiesel to serve as tracking agents. Immersing a polypropylene sample in biodiesel and computing the difference in levels of these trace chemical species over time (relative to the control) indirectly reflected the degree of adsorption and desorption. These particular trace species were selected because they tend to be absent

in most polymers so the study could be free of undesirable matrix effects. Species of major elements such as sodium or magnesium were avoided because they tend to be present as impurities in most materials and could affect the results of the study. Measurement of the species of interest was undertaken by a hyphenated facility combining high performance liquid chromatography with inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [13,14]. The system has a built-in dynamic reaction cell (DRC) for superior results, and possesses the special ability of isolating all four species [Cr³⁺/Cr⁶⁺ and As³⁺/As⁵⁺] concurrently in a single run followed by high resolution mass detection [15-17]. In the HPLC unit, retention times interfere with the separation process but this does not create a setback because complete separation is attained when the species in question are conveyed via quadrupole selection to the mass detector. The system itself is unique as the mass detector acquires the data individually through two mass channels (m/

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$z=52$ for Cr⁺ and $m/z=91$ for AsO⁺) thus making concurrent elution possible. Hence overlap of retention times can be completely ruled out with this multiple arrangement. This simultaneous detection system renders the measurement fast and the electron multiplier unit ensures high sensitivity and accuracy.

Two batches of neem biodiesel used in this investigation were prepared in our laboratory- one from natural neem seeds and the other from locally procured neem oil. We discovered that samples prepared from the local neem oil feedstock were infected with low levels of water and were conveniently used to determine whether water influenced the rates of adsorption and desorption. The study makes a marked contribution to research in materials science.

Materials and Methods

Sample preparation/liquid chromatography

Samples of neem oil were obtained locally from retail outlets and converted to biodiesel using standard catalysts NaOH and KOH [18-20]. A similar process was undertaken for extracting biodiesel from neem seeds [10,21]. The physical properties of both batches of samples conformed to international standards [18,22]. However, the biofuel from commercial neem oil feedstock was found to contain marginally higher water content (0.9%) and was employed in the study to evaluate the effect of water on the results. For the purpose of adsorption/desorption experiments polypropylene materials doped with minor levels of Mg, Ti and Zn to simulate catalytic impurities were used. Identical samples of polypropylene (60 × 14 × 2 mm) were immersed in polypropylene jars containing neem biodiesel for a period of 24 weeks. Minor quantities of this biodiesel were removed from the beakers and analyzed at selected intervals. Results were compared with a control. A Perkin Elmer instrument (Figure 1) was employed for isolation of all four species: Cr³⁺/Cr⁶⁺ and As³⁺/As⁵⁺. The stationary phase was composed of deactivated silica, pore size: 5 μm; and consisted of a 150 mm column (C8)-internal diameter, 4.6 mm. The mobile phase was a homogeneous solution of pH 7.2 (adjusted with dilute aqueous HNO₃/NH₄OH) composed of 1 × 10⁻³ M TBAH, 0.5 × 10⁻³ EDTA and 5% aqueous methanol. The system is equipped to handle multiple samples, with an optimal elution rate of 1.2 mL/min. Details for preparing the mobile and stationary phases appear in Perkin Elmer reports on the subject [23] and were adopted for purposes of optimization [13]. The system was calibrated using certified standards obtained from VHG Labs.

Dynamic reaction cell (DRC) / plasma mass spectrometry

Mass separation of the isolated species was attained with a quadrupole selector in a Perkin Elmer SCIEX DRC-e ICP-MS fitted with a dynamic reaction cell (DRC) (Figure 1). The nebulizer gas was

0.80 L/min and the oxygen flow in the DRC was 0.4 mL/min. The function of the DRC was to reduce interferences by interaction of the eluted species with the oxygen flow gas. Cr⁺ was detected at m/z 52; and As⁺ was detected as an adduct ion, AsO⁺, m/z 91, after reacting with oxygen. The ICP-MS was calibrated with certified standards (Fluka 70007; 10.00 ppb per element); and repeatability studies produced relative standard deviations <5% indicating that the system performed satisfactorily (Table 1). Drift in instrumental performance was corrected by use of an internal standard. Samples and standards were all made up in aqueous solution consistent with the mobile phase. The software adjusted for random matrix effects.

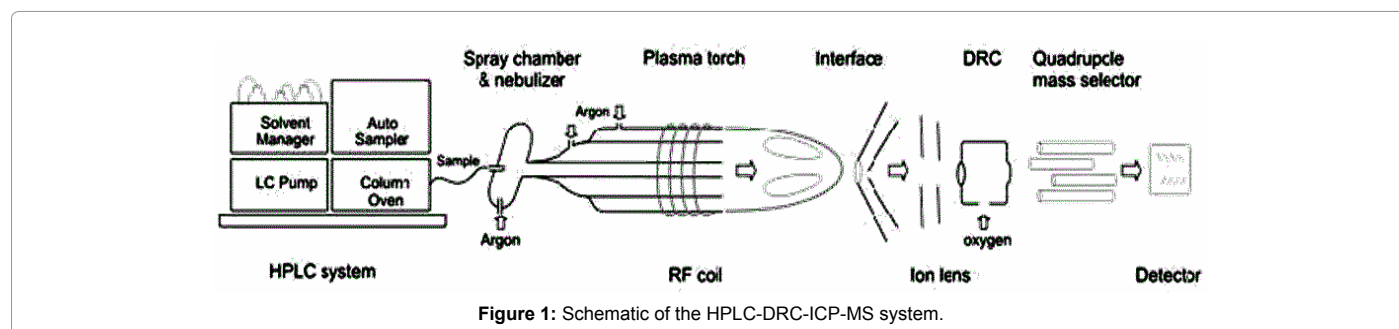
Results and Discussion

Collision cell/retention times

The notion of combining a collision cell or dynamic reaction cell with HPLC/plasma mass spectrometry is to resolve the overlap in retention times that are encountered when all four species of interest are simultaneously eluted from a conventional chromatographic column. Interfering retention times make regular analysis almost impossible and conventional liquid chromatographic techniques fail to conveniently distinguish all four species in a single run. In the present study, the recorded retention times (min) were as follows: As³⁺: 1.61; As⁵⁺: 4.06; Cr³⁺: 3.71; Cr⁶⁺: 5.80. Inspection of Figure 2 clearly indicates that As⁵⁺ overlaps with Cr³⁺; and as it tails off the tail-end of its peak structure interferes with Cr⁶⁺. A point to note is that asymmetry in peak structure was optimized for favorable results by adjusting the instrument settings according to standard protocol [24]. The proximity of the chromatograms displayed in Figure 2 reveals that de-convoluting the data to provide a meaningful analysis would be futile, and the only possible solution of attaining distinct resolution would be to transport the eluted species to an ICP equipped with a DRC. It is necessary to emphasize that the technique employed here using the DRC for ultimate mass detection is a unique way of clearly differentiating between all four species. The cell itself functions by utilizing a flow of oxygen to either dissociate interfering species or to coalesce with the species of interest for suitable resolution. For instance ArC⁺ (present at m/z 52) created within the plasma itself interferes with Cr⁺ at m/z 52. Oxygen gas in the DRC dissociates ArC⁺ and thus suppresses the interference. On the other hand, As⁺ (at m/z 75) binds to oxygen to form a complex adduct, and is detected at m/z 91, thus overcoming interferences from instrumental species ArCl⁺ and CaCl⁺ that also occur at m/z 75. A quadrupole selector built into the system steers the charged species to a mass detector for clear resolution and easy detection. The system is ultra-sensitive and can cope with high sample throughput and low sample volumes (50 μL).

Adsorption/desorption effects

The idea of using four separate markers (Cr³⁺/Cr⁶⁺ and As³⁺/As⁵⁺)



Element	Trial #1	Trial #2	Trial #3	Mean	SD	SD %
V	10.01	9.36	9.82	9.73	0.33	3.43
Cr	9.51	10.04	10.07	9.87	0.32	3.19
Co	10.54	9.82	10.12	10.16	0.36	3.56
Ni	10.08	9.46	9.56	9.70	0.33	3.43
As	9.82	10.21	9.74	9.92	0.25	2.53
Se	9.78	9.59	9.61	9.66	0.10	1.08
Cd	9.51	10.06	10.09	9.89	0.33	3.30
U	10.08	9.65	10.12	9.95	0.26	2.62

Table 1: Repeatability test of the ICP-MS for various elements (µg/L) in an aqueous standard showing the mean, standard deviation (SD) and relative standard deviation (SD%).

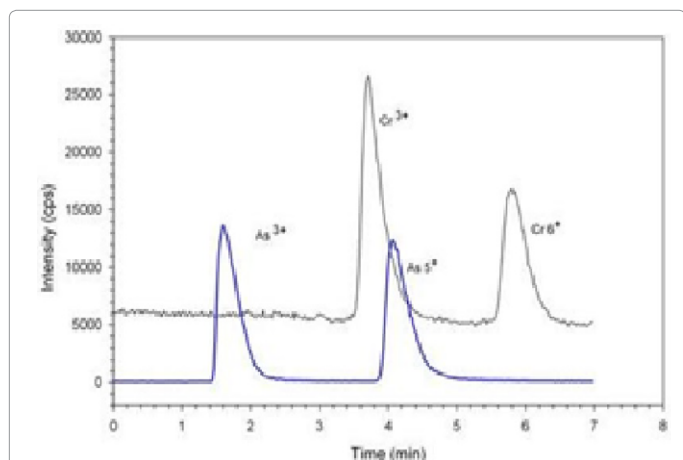


Figure 2: Typical HPLC chromatograms showing retention times for As³⁺ /As⁵⁺ and Cr³⁺ /Cr⁶⁺.

was to evaluate the consistency of adsorption/desorption behavior over the experimental period. Metal and metalloid species were purposefully selected to establish if different trends existed with different species. It is necessary to underscore that these phenomena were indirectly reflected as the difference in constituent trace levels between the experimental and control samples. The data are depicted in Figure 3 for the “wet” and “dry” samples. The Cr³⁺ and Cr⁶⁺ plots delineate similar trends with continuous adsorption up to week 18 followed by gradual desorption. In the Cr³⁺ plot the water infected sample shows more marked adsorption than the dry sample. This pattern is reversed in the Cr⁶⁺ plot. For an interpretation of this converse effect it is necessary to refer to the aquo-complexes of these species [24,25] in Figure 4. In Figure 4 Cr³⁺ complexes with six water molecules, while Cr⁶⁺ complexes with only four. The data therefore, suggest that on a microscopic scale the specie linked to more water molecules displays more pronounced adsorption, due probably to the adhesive effect of water on polypropylene. Subsequent interfacial electrostatic repulsion between Cr³⁺ and Cr⁶⁺ aquo-complexes could account for the reversal in trend in Figure 3. The exchange between water molecules and the interplay of intermolecular forces is perpetual [14] and it would seem from the data that biodiesel “free” from water contamination adheres to a lesser extent on the polypropylene. One possible explanation could be that the presence of water contamination enhances the hydrophilic environment and encourages adsorption. Interestingly, the pattern depicted by the overall data suggest that consistent adsorption takes place and tends to be more marked than desorption after about 18 weeks. The As³⁺ /As⁵⁺ plots in Figure 5 display similar trends. Adsorption phenomena for the arsenic species are less pronounced and could be due to their metalloid nature [26].

Kinetics

Biofuels are known to gradually erode polymeric material on contact. There is no known documented method to determine the rates at which biofuels adsorb and desorb from polymer surfaces. However, these effects can be indirectly established by measuring the rates at which chemical species in biodiesel adhere and separate at the interface of fluid and polymer surface.

The kinetics of the study was derived from concentration-time curves (Figure 3) and reflects cycles of growth and decay. The growth represents adsorption effects; and decay reflects desorption. The rationale behind using a water infected sample was to probe the effect of charge and ionic radii in a hydrophilic environment. The chemical species of interest possess the following ionic radii: As³⁺: 64 pm; As⁵⁺: 60 pm; Cr³⁺: 64 pm; and Cr⁶⁺: 52 pm. With reference to Figure 5 the growth and decline of the plots indirectly delineate the respective rates of adsorption and desorption. It was established that the recorded data followed first-order kinetics [26]. The question to ask is: “Does charge affect the kinetics of the study?” Clearly from the plots in Figure 5 the species with the lowest ionic radii and highest charge display the sharpest adsorption rates in the water contaminated samples. This suggests that the highly polar nature of water and the interplay of hydrogen bonding and ion-dipole interactions feature distinctly in contributing to adhesion to the polypropylene surface. Highly charged species are smaller and can coalesce more strongly with the less bulky water molecule [27] to form a potent “sticking complex” leading to more pronounced adsorption effects. These effects are less prominent in biodiesel *per se* resulting in gentler curves as depicted in Figure 5. In water infected biodiesel adsorption rate constants were between 0.3–0.5 wk⁻¹ for Cr⁶⁺ and As⁵⁺. The remaining rate constants were lower and dropped to about 0.1 wk⁻¹ for all other plots in Figure 5. An interesting feature is that desorption is almost

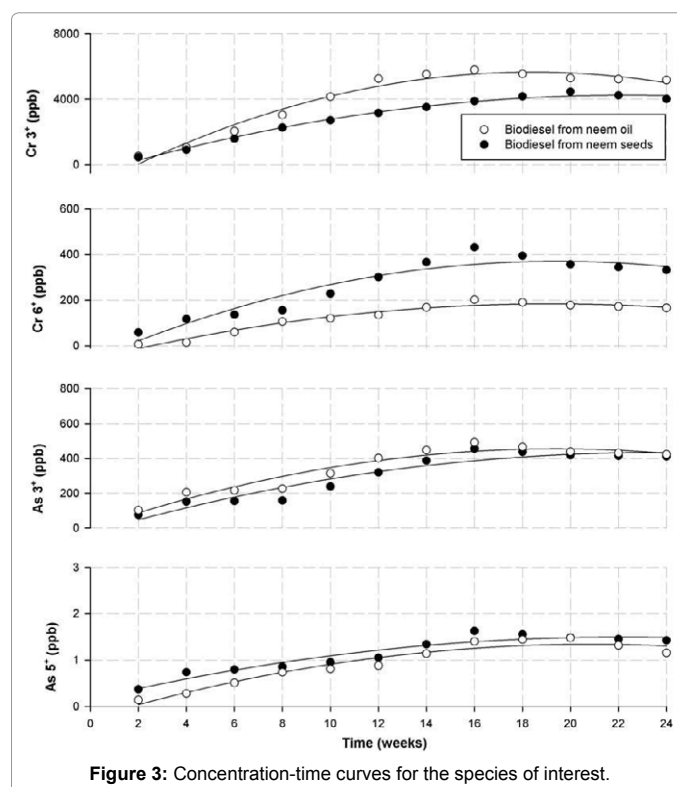
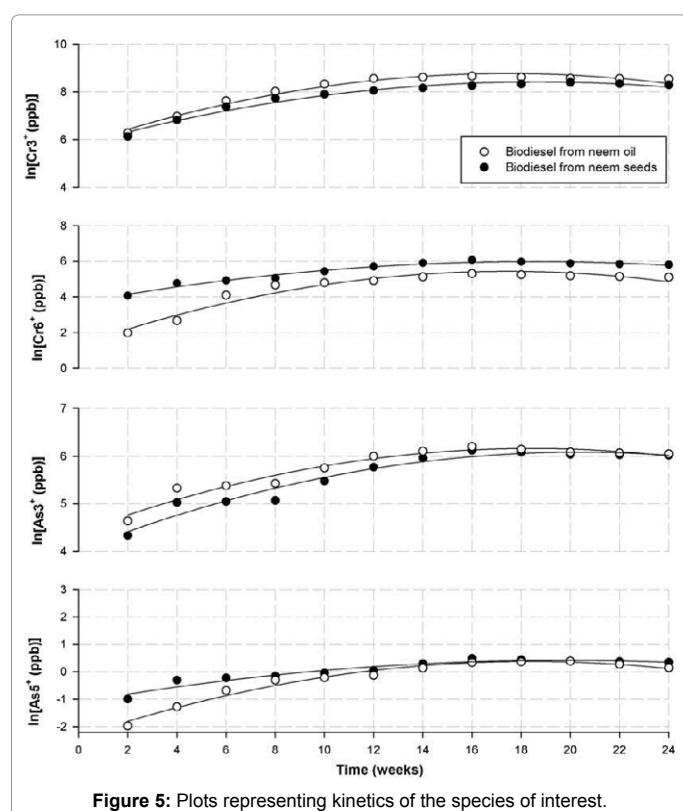
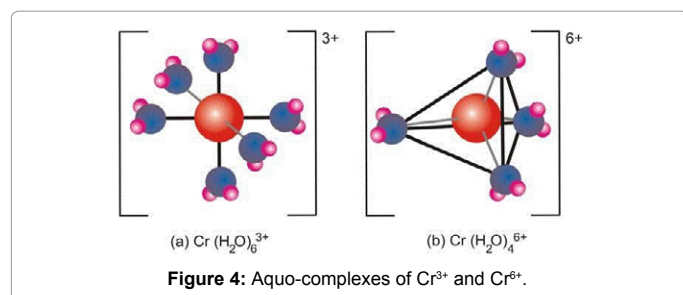


Figure 3: Concentration-time curves for the species of interest.



imperceptible in some cases (with considerably lower rate constants) suggesting that attrition is a chronic effect.

Impact of the study

The foremost impact of our study is that we have developed a novel technique using natural tracers or markers in biodiesel to establish adsorption and desorption effects. The nature of our study is such that it could be extended to polymeric materials in general. It is evident from the plots in Figures 3 and 5 that the trends in adsorption/desorption are consistent denoting sharper adsorption than desorption in all cases. The data also suggest that the adhesion to polymeric material is long-term and would have a definite effect on the properties of the material over time. Fraying of polymer fittings in vehicles could result from this chronic adhesion of biofuels on their surfaces. The data in Figure 5 demonstrate that the rates of adsorption are sharper in the presence of water contamination. The inference therefore, is that the damage that biofuels could inflict, in general, could be substantially reduced by minimizing the water content in biodiesel. It must be understood that it is not possible to have no water at all in biodiesel due to the nature of the trans-esterification process. However, water contamination is detrimental and high quality biodiesel could reduce attrition of polymeric materials.

Of considerable significance is that the technique applied to concurrently determine all four species was both unique and sensitive. Under normal circumstances these species cannot be simultaneously determined with any contemporary analytical method. Standard HPLC is unable to resolve all four species distinctly. The combination of the dynamic reaction cell with HPLC-ICP-MS provided the necessary sensitivity and recourse for swift and accurate differentiation of these species.

Conclusion

The use of intrinsic markers: Cr³⁺/Cr⁶⁺ and As³⁺/As⁵⁺ to provide an insight into the kinetics of adsorption/desorption phenomena associated with polypropylene in neem biodiesel has not been previously reported and breaks new ground in the area of materials research. It was found that the rates of adsorption were more marked than the desorption rates, especially in water-contaminated samples. This was attributed to the hydrophilic nature of the environment and denoted that contaminated biodiesel could lead to more pronounced attrition. The technique employed in this study (DRC-HPLC-ICP-MS) was complex with multiple features and displayed high performance with ultra-sensitivity. The study could be extended to polymers in general and would make a significant contribution to materials research.

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