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Catalytic effects of period iv transition metal in the oxidation of biodiesel

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**CATALYTIC EFFECTS OF PERIOD IV TRANSITION
METALS IN THE OXIDATION OF BIODIESEL**

by

BRADLEY R CLARK

THESIS

Submitted to the Graduate School

of Wayne State University,

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TECHNOLOGY

Approved by:

Advisor

Date

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Chapter 1 Introduction

Biodiesel is a major source of liquid biofuels. The consumption of biodiesel has experienced strong growth in recent years but, fuel quality problems have been reported. Biodiesel, like any other hydrocarbon fuel, can react with dissolved oxygen resulting in fuel quality degradation (oxidation). Among the problems reported are increased total acid number (TAN) leading to fuel system corrosion (figures 1 and 2), increased viscosity and the formation of solids leading to injector fouling.[1-13].



Figure 1
Upper half of fuel tank



Figure 2
Lower half of fuel tank

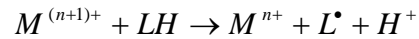
Factors that increase the rate of oxidation include light, heat and metallic contaminants.[14-18] Metals function as catalysts by accelerating the rate of reaction between biodiesel and oxygen, In this study the catalytic effects of period IV transition metal ions are investigated. The rate of oxidation was determined by the Rancimat induction period test.

Oxidation

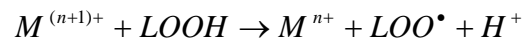
The reaction of biodiesel with oxygen proceeds by a mechanism known as free radical oxidation. A free radical is an organic molecule, typically containing oxygen, with an unpaired electron. Since electrons normally form bonding pairs, this singular electron is highly reactive. Free radical oxidation contains three distinct steps: initiation, propagation and termination. Initiation is the formation of a free radical by breaking a chemical bond. In the examples discussed here it is typically a hydrogen - carbon or

hydrogen - oxygen bond that is broken. Propagation is the continuous generation of more free radicals. Termination is a reaction between free radicals or between a free radical and an antioxidant that eliminates the unpaired electron. Catalytic metals promote free radical oxidation by transferring electrons. This results in a change of oxidation state of the metal ion. Reactions demonstrating the steps of free radical oxidation are given below.

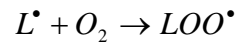
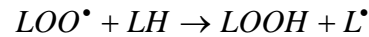
Alkyl Initiation



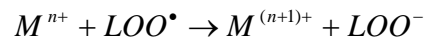
Peroxy and alkoxy initiation



Propagation



Termination



Legend

M^{n+} metal ion

LH biodiesel

$LOOH$ hydroperoxide

$L^{\bullet}, LO^{\bullet}, LOO^{\bullet}$ free radicals

H^+, OH^-, LOO^- ions

Bis-allylic structure

Biodiesel is a mixture of fatty acid methyl esters (FAME). The vegetable oils used to produce biodiesel contain a mixture of saturated and unsaturated fatty acids. Chief

among the unsaturated fatty acids are oleic, linoleic and linolenic acids.[14-16] These are relevant to the study of free radical oxidation because unsaturated fatty acids contain weak carbon – hydrogen bonds at specific locations. These locations are adjacent to a carbon – carbon double bond. See Figure 3. The hydrogen at this location is called “allylic”. A carbon – carbon double bond lowers the strength of the carbon – hydrogen bond at the allylic location.[14-16] Less energy is required to break an allylic hydrogen bond and produce a free radical. Figure 4 shows linoleic acid. This molecule contains two double bonds with a “twice” allylic hydrogen between them. This location is called “bis-allylic” and the carbon - hydrogen bond energy is even lower than at the allylic.[14-16] As expected the formation of a free radical at the bis-allylic location requires less energy than the allylic location. Figure 5 show the structure of linolenic acid with three double bonds and two bis-allylic sites. Linolenic acid is the most reactive of the three and purified samples are pyrophoric (i.e. spontaneously combust in air.)

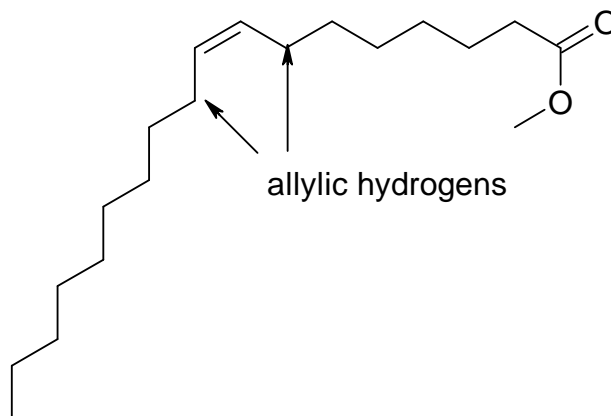


Figure 3
Methyl Oleate with allylic but no bis-allylic hydrogen atoms

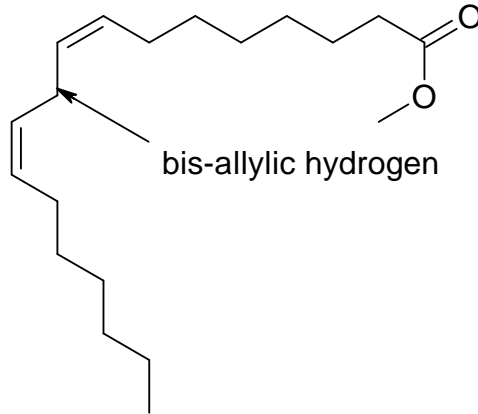


Figure 4
Methyl Linoleate with one bis-allylic hydrogen atom

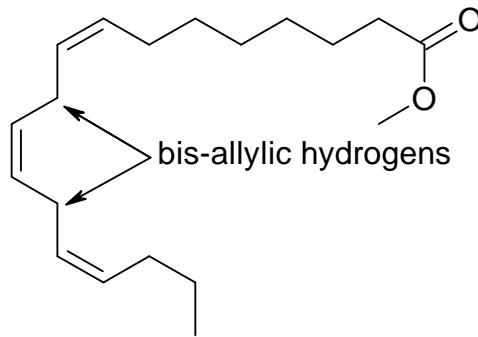


Figure 5
Methyl Linolenate with two bis-allylic hydrogen atoms

Metals

There are many reports of detrimental interactions between metals and biodiesel (B100) or biodiesel blends. Copper and copper alloys are reported as being highly catalytic. The effects of increased oxidation include severe corrosion, heavy gum formation, and increases of peroxide value, total acid number (TAN) and viscosity. [2, 7, 18-20] Copper and its alloys are also reported to reduce the induction period as

determined by the Rancimat or oxidative stability index (OSI). [8, 21] Fe and steel are reported to cause increases of TAN, peroxide value and viscosity with a decrease of induction period. [7, 8, 19-21] Aluminum and aluminum alloys are reported to cause an increase of TAN and a decrease of induction period. [8, 19] Tin, zinc and nickel are all reported to reduce induction period.[7, 8, 21] Recent work studied the effect of powdered metals on the OSI of methyl oleate. Reductions of OSI were reported after additions of powdered copper, powdered iron and powdered nickel.[21]

Metal Ions

There are many reported interactions of metal ions with triglycerides, fatty acids and fatty acid methyl esters (biodiesel). Metal ions are catalytic for the initiation and propagation stages of free radical oxidation.[14, 18, 22-24] In triglycerides and fatty acids, the detrimental effects of copper and iron catalysis have been described.[18, 24-26] The reported effects are an increase of peroxide value and decrease of induction period.[26] The maximum reported decreases of induction period are 40% for iron and 80% for copper. The catalytic effects of cobalt, manganese and nickel are also reported.[18, 24, 27] In biodiesel, the catalytic effects of copper and iron are reported frequently. [7, 9, 28-30] The effects include an increase in carboxylic acid formation [28] and a reduction of induction period [30]. There are reports that indicate there is no direct correlation between iron concentration and induction period although iron does catalyzed hydroperoxide decomposition (i.e. propagation). [9, 28] Since biodiesel is most often used in blends, catalytic metals could be introduced from petroleum diesel fuel. Transition metals at ppm levels in petroleum diesel from Asia have been reported.[31]

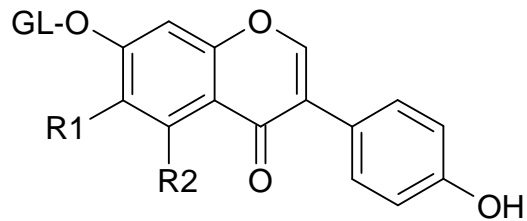
Catalytic metal ions may be intentionally added as diesel particulate filter additives. These include cerium, copper, iron, lead, manganese, nickel and strontium.[30, 32-34] The ability of cerium, copper and iron fuel additives to reduce biodiesel induction period has been reported.[30]

This brief literature review indicates that the catalytic effects of transition metal ions on the oxidative stability of biodiesel have not been fully elucidated. While these reports indicate the catalytic effects of different metals, the choice of metals was sporadic and the concentration ranges are limited. The period IV transition metal ions selected for investigation in this work are: V, Cr, Mn, Fe, Co Ni, Cu and Zn. The catalytic effects of Mn, Fe, Co, Ni, Cu and Zn ions have been previously reported although there was little or no attempt to determine the effect of concentration on the rate of oxidation. Zn was added because the catalytic effects of the metal have been reported and because it is present in brass fittings. Cr was added because it is present in stainless steel. V was added because of its presence in crude petroleum. [35] The metals were added as hydrated nitrate or chloride salts pre-dissolved in anhydrous methanol. Since previously reported work used metals or organic metal salts, the effects of these inorganic counter-ions will be investigated. The effects of small additions of water are also investigated.

Antioxidants

The rate of biodiesel oxidation is influenced by the presence of naturally occurring antioxidants. [9, 14, 16, 36] The specific antioxidants and their concentrations

vary with feedstock. In this study, biodiesel from two different feedstocks were tested: soybean oil and cottonseed oil. The Rancimat induction period is essentially a measure of the ability of a biodiesel sample to resist free radical oxidation. The presence of naturally occurring antioxidants will increase the induction period. Antioxidants found in vegetable oils would transfer to FAME (biodiesel) during transesterification. These naturally occurring antioxidants can be separated into two broad categories: tocopherols and isoflavones. Tocopherols decompose readily in the presence of oxygen and would not be expected to offer significant protection during the Rancimat test.[36, 37] The difference between the Rancimat results of soybean oil and cottonseed oil may be attributed to the differences in naturally occurring antioxidants including isoflavones. Their chemical structure is given in Figure 6. There is precedence for this interpretation in the literature.[38, 39] Quercetin and kaempferol are typical isoflavones found in cottonseed.[40] Daidzein and genistein are typical isoflavones found in soybeans.[41] Isoflavone may function to inhibit free radical oxidation in two ways. They may function as peroxy-radical scavengers and thus terminate the sequence of free radical oxidation.[18, 42-44] They may also function as chelators, binding transition metals into stable complexes thereby inhibiting catalysis.[43, 44]



Genistein R1 = H, R2 = OH
 Daidzein R1 = H, R2 = H
 Glycitein R1 = OCH₃, R2 = H

Figure 6
 Soybean isoflavone glycosides

The varieties and concentrations of different isoflavones present in biodiesels of different feedstocks is an open question. Variations in triglyceride feedstock will inevitably produce variations in the biodiesel manufactured from it. Variations in the method of manufacture must also be considered. An attempt to make broad generalizations about antioxidant concentrations in currently produced biodiesel is problematic. Yet, the capacity of different isoflavones to act as metal chelators and free radical chain terminators could explain the differences observed between biodiesels of different feedstocks.

The objectives of this research are to determine: 1) to what extent are V, Cr, Mn, Fe, Co Ni, Cu and Zn catalytic for biodiesel oxidation, 2) what is the relationship between metal ion concentration and induction period and 3) do these metals react differently in biodiesel from different feedstocks?

Chapter 2 Materials and Methods

Reagents

The Table 1 lists the sources of the ions investigated in this study:

Ion	Source	Purity and Supplier
V (II)	Vanadium (II) chloride	85% Aldrich
Cr (III)	Chromium (III) chloride hexahydrate	≥98.0% Sigma-Aldrich
Mn (II)	Manganese (II) chloride tetrahydrate	98+% A.C.S. Reagent Sigma-Aldrich
Fe (III)	Iron (III) nitrate nonahydrate	98+% A.C.S. Reagent Sigma-Aldrich
Co (II)	Cobalt (II) nitrate hexahydrate	98+% A.C.S. Reagent Sigma-Aldrich
Ni (II)	Nickel (II) nitrate hexahydrate	E M Science
Cu (III)	Copper (III) nitrate	98+% A.C.S. Reagent Sigma-Aldrich
Zn (II)	Zinc (II) nitrate	98+% A.C.S. Reagent Sigma-Aldrich

Table 1
Sources of metal ion studied in this research

Stock solutions of each metal were prepared by dissolving the required salt in certified A.C.S. Spectranalyzed® anhydrous methanol in 100 ml volumetric flasks. Glass stoppers were used to inhibit oxidation of reduced metals by dissolved air. All solutions were stored in a closed cabinet at room temperature.

Biodiesel

Biodiesel from soybean oil and cottonseed oil feedstocks were obtained from Biodiesel Industries (Denton, Texas). Samples of each feedstock were transferred from 50 gallon drums to air-tight steel one gallon containers and were stored at 4 C in a commercial refrigerator. The distribution of fatty acids for these biodiesels is given in Table 2. These values are typical values for these feedstocks. The IP, TAN and viscosity are given in Table 3 and again are typical values.

BDI	Soybean	Cottonseed
C14:0	0.00%	0.76%
C16:0	13.72%	24.60%
C16:1	0.68%	0.37%
C18:0	5.01%	2.67%
C18:1	24.61%	18.35%
C18:2	47.40%	52.70%
C18:3	5.92%	0.00%
C20:0	0.00%	0.00%
C22:1	0.00%	0.00%
SUM	97.33%	99.45%

Table 2
Fatty acid methyl ester distribution

	IP	TAN	Viscosity
units	hr (110 °C)	mg KOH/g	cSt (40 C)
BDI Soybean	3.5	0.176	4.321
BDI Cottonseed	6.57	0.262	4.221

Table 3
Biodiesel properties

Instrumentation

Induction period is determined by the 743 Rancimat manufactured by Metrohm Ion analysis.

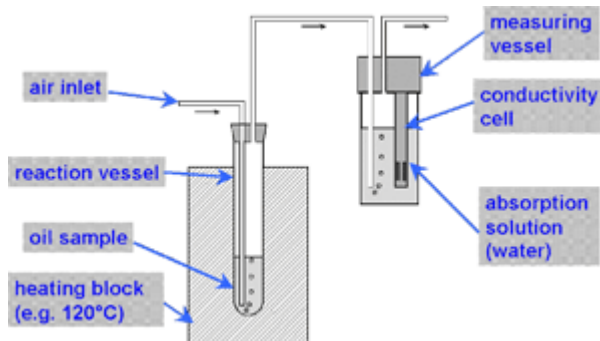


Figure 7
Schematic of Rancimat induction period tester

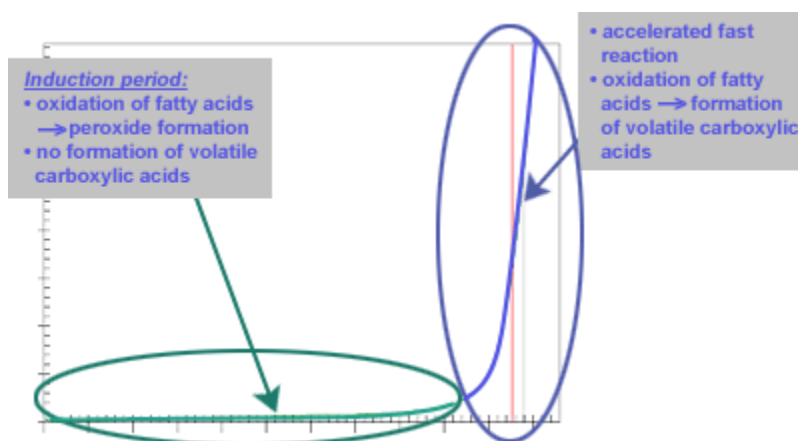


Figure 8
Rancimat oxidation curve

Induction Period Standard

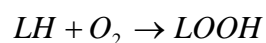
The most important test for the study of catalytic metal effects in biodiesel is the induction period (IP) determination. [45] The use of the Rancimat to determine oxidative stability is described in DIN EN 14112 and ASTM Specification D6751. The Rancimat determines the ability of a sample to resist oxidation under conditions of heat and continuous air flow.[46] (See figure 7.) It is an accelerated test designed for direct comparison between samples and produces results that are qualitative, not strictly quantitative. It measures induction period by determining the point of the maximum rate of change in accumulated oxidation products. (See figure 8.) According to the procedure described in DIN EN 14112, 3 grams of biodiesel were weighed into a reaction vessel. The appropriate amount of metal was added volumetrically by micropipette to the 3 gram sample. After metal additions, the reaction vessels were swirled to ensure good mixing and were placed in the Rancimat. The time delay between metal addition and the beginning of the Rancimat test did not exceed 20 minutes. The temperature during the Rancimat test was 110 C with a continuous air flow of 10 liters per hour, as required by the specification. Samples of a specific metal/feedstock combination were run in triplicate with blanks run in duplicate.

Chapter 3 Mathematical Modeling

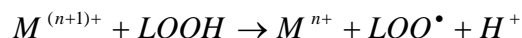
Generic Model

In this section a mathematical model relating metal concentration and induction period for all choices of metal and feedstock is determined. This model must conform to the kinetics of the metal catalyzed free radical oxidation reactions described in the literature.[14-16, 47] Therefore, it is important to review the published results on the mechanisms of metal catalysis of hydroperoxide free radical oxidations. Transition metals may catalyze reactions in both the initiation and termination stages.[22, 48, 49]

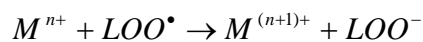
Hydroperoxide formation



Peroxy initiation

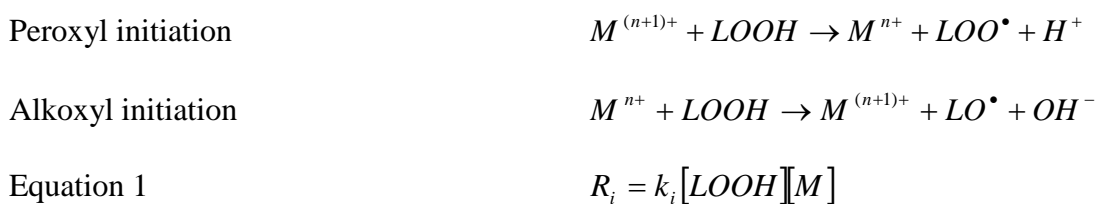


Termination



Note that $M^{(n+1)+}$ denotes a higher oxidation state of the metal ion and M^{n+} denotes a lower oxidation state. It may be possible that the difference in valence states is greater than one. Metal catalysis of hydroperoxide decomposition has been frequently described in the literature on biodiesel.[9] While metal catalysis of alkyl initiation and termination has been discussed in the foods industry, these reactions have not been applied to an analysis of the Rancimat induction period data.

The initial kinetics analysis will focus on the metal catalysis of the hydroperoxide initiation and termination stages of free radical oxidation. A kinetics analysis of metal catalysis of the propagation stage of free radical oxidation will be added later. This analysis begins by assuming steady state conditions. Thus, the rate of free radical initiation equals the rate of termination. The initiation reaction and the corresponding rate equation is given below:



R_i is the rate of free radical initiation, k_i is the rate constant, $[LH]$ is the molar concentration of bis-allylic FAME, $[M]$ is the molar concentration of metal ion, and $[LOOH]$ is the molar concentration of hydroperoxide containing FAME. Note that the rate constant k_i is the sum of peroxy and alkoxy initiations.

The termination of the free radical chain can proceed by a variety of reactions. These include: 1) peroxy to peroxy termination, 2) peroxy to antioxidant termination, 3) peroxy to alkyl termination and 4) peroxy to alkoxy termination. Metal catalyzed termination reactions are not considered in this analysis. The rate equations for the four termination reactions are given below:

$$R_{t1} = 2k_{peroxide} [LOO\cdot]^2$$

$$R_{t2} = k_{peroxide} k_{antioxidant} [LOO\cdot] [AH]$$

Four termination reactions

$$R_{t3} = k_{peroxide} k_{alkyl} [LOO\cdot] [L\cdot]$$

$$R_{t4} = k_{peroxide} k_{alkoxyl} [LOO\cdot] [LO\cdot]$$

R_t is the rate of termination, $LOO\cdot$ is the peroxy radical, AH is the antioxidant, $L\cdot$ is the alkyl radical and $LO\cdot$ is the alkoxy radical. The different k_i 's are the corresponding rate constants. Note that 1) and 4) produce multiple oxygen to oxygen bonds which are unstable and lead the rapid molecular rearrangements and breakdown products.[14, 47]

The analysis proceeds by assuming steady state conditions (i.e. that the rate of initiation is equal to the rate of termination.) Then substitute the different termination rates described above.

$$R_i = R_t$$

$$R_i = R_{t1} + R_{t2} + R_{t3} + R_{t4}$$

$$k_i [LOOH] [M] = 2k_{peroxyl} [LOO\cdot]^2 + k_{peroxyl} k_{antioxidant} [LOO\cdot] [AH] + k_{peroxyl} k_{alkyl} [LOO\cdot] [L\cdot] + k_{peroxyl} k_{alkoxyl} [LOO\cdot] [LO\cdot]$$

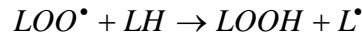
$$k_i [LOOH] [M] = 2k_{t1} [LOO\cdot]^2 + k_{t2} [LOO\cdot] [AH] + k_{t3} [LOO\cdot] [L\cdot] + k_{t4} [LOO\cdot] [LO\cdot]$$

The previous equation may be solved for peroxy radical concentration by the quadratic equation.

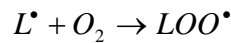
$$[LOO^{\bullet}] = -\frac{1}{4k_{t1}} \left(k_{i2}[AH] + k_{i3}[L^{\bullet}] + k_{i4}[LO^{\bullet}] \pm \left(k_{i2}^2[AH]^2 + 2k_{i2}k_{i3}[AH][L^{\bullet}] + 2k_{i2}k_{i4}[AH][LO^{\bullet}] + k_{i3}^2[L^{\bullet}]^2 \right)^{1/2} \right)$$

Equation 2

Initiation and termination have been considered. Next the mechanism of hydroperoxide propagation must be considered.



Propagation



Where LH is the bis-allylic hydrogen site of the unsaturated fatty acid. The reaction of bis-allylic alkyl radical with oxygen is reported to be very fast.[14, 47] The extraction of bis-allylic hydrogen is slower and rate determining. Using this mechanism as a guide, the rate of change of hydroperoxide concentration over time is given as:

$$\frac{d[LOOH]}{dt} = k_{prop} [LOO^{\bullet}] [LH]$$

Equation 3

Where k_{prop} is the rate constant of propagation.

Substitute the solution of the peroxy radical concentration (equation 2) into the rate of change of hydroperoxide concentration over time (equation 3) results in a separable equation that may be integrated.

$$\int d[LOOH] = \int k_{prop}[LOO^*][LH]dt$$

$$\int d[LOOH] = \int k_{prop} \left\langle -\frac{1}{4k_{i1}} \left(k_{r2}[AH] + k_{r3}[L^*] + k_{r4}[LO^*] \pm \left(k_{r2}^2[AH]^2 + 2k_{r2}k_{r3}[AH][L^*] + 2k_{r2}k_{r4}[AH][LO^*] + k_{r3}^2[L^*]^2 \right)^{1/2} \right) \right\rangle [LH] dt$$

When solved for the metal concentration the result is equation 4.

$$[M] = \frac{2k_{peroxy}[LOOH] + k_{prop}k_{anti}[LH][AH]t + k_{prop}k_{alkyl}[LH][L^*]t + k_{prop}k_{alkoxy}[LH][LO^*]t}{k_{initiation}k_{prop}^2[LH]^2t^2} + C$$

Equation 4

In this equation, C is the constant of integration. The metal concentration is the exogenous variable and time (i.e. induction period) is the endogenous variable. Solving for time instead of metal produces equation 5. The lack of information on the rate constants and concentration of the different species make the use of this equation unrealistic.

$$t = - \frac{4k_{i1}[LOOH]}{\left(k_p[LH] \left(k_{r2}[AH] + k_{r3}[L^*] + k_{r4}[LO^*] - \left(k_{r2}^2[AH]^2 + 2k_{r2}k_{r3}[AH][L^*] + 2k_{r3}k_{r4}[AH][LO^*] + k_{r3}^2[L^*]^2 \right)^{1/2} \right) \right)}$$

Equation 5

Applied Model

The right hand side of Equation 4 may be separated into two terms and a constant.

$$1^{\text{st}} \text{ term} \quad \frac{2k_{\text{peroxyl}}[\text{LOOH}]}{k_{\text{initiation}}k_{\text{prop}}^2[\text{LH}]^2t^2}$$

The first term is a function of the inverse square of time: $\frac{1}{t^2}$. This term must be positive since all constants and concentrations are greater than zero.

$$2^{\text{nd}} \text{ term} \quad \frac{k_{\text{prop}}k_{\text{anti}}[\text{LH}][\text{AH}] + k_{\text{prop}}k_{\text{alkyl}}[\text{LH}][\text{L}^\bullet] + k_{\text{prop}}k_{\text{alkoxyl}}[\text{LH}][\text{LO}^\bullet]}{k_{\text{initiation}}k_{\text{prop}}^2[\text{LH}]^2t}$$

The second term is a function of the inverse of time: $\frac{1}{t}$. Consider the different concentrations in the 2nd term. The concentration of antioxidant will be zero at the end of the test (i.e. $[\text{AH}] = 0$ when $t = \text{IP}$.) The concentration of alkyl radical $[\text{L}^\bullet]$ will be near zero since the Rancimat test uses a continuous flow of air into the reaction vessel and the rate of reaction of alkyl radical with oxygen to form peroxy radicals is very fast.[14]

$$2^{\text{nd}} \text{ term simplified} \quad \frac{k_{\text{prop}}k_{\text{alkoxyl}}[\text{LH}][\text{LO}^\bullet]}{k_{\text{initiation}}k_{\text{prop}}^2[\text{LH}]^2t}$$

What remains is a function of alkoxy radical $[LO^\bullet]$ and bis-allylic hydrogen $[LH]$. The concentrations of these are unknown and the concentrations will change over time. This is not a problem since the concentrations at the end of the test (time equals induction period) is the only time of interest in these experiments. In both the 1st and 2nd terms all quantities should be positive.

Let $t = IP$. Collect all constants and concentrations in the 1st term and designate them as k_2 . Collect all constants and concentrations in the 2nd term and designate them as k_1 . Designate the constant of integration as k_0 . An equation of the algebraic relationship between metal concentration and induction period has the following general form:

$$[M] = \frac{k_2}{IP^2} + \frac{k_1}{IP} + k_0$$

Equation 6

This equation will be referred to as the “general form equation”. This equation shows that IP must decrease as metal concentration increases.

Chapter 4 Data

Metal concentration ranges

Ion	Concentration range in soybean biodiesel	concentration range in cottonseed biodiesel
V (II)	0.1 – 5.0 ppm	0.1 – 1.0 ppm
Cr (III)	0.1 – 1.0 ppm	0.1 – 1.0 ppm
Mn (II)	0.5 – 5.0 ppm	0.2 – 5.0 ppm
Fe (III)	2 – 60 ppm	10 – 80 ppm
Co (II)	0.1 – 1.0 ppm	0.05 – 0.5 ppm
Ni (II)	2 – 60 ppm	5 – 40 ppm
Cu (III)	0.02 – 2.0 ppm	0.025 – 0.2 ppm
Zn (II)	0.5 – 10.0 ppm	1.0 – 8.0 ppm

Table 4
Concentration ranges of metal additions

Table 2 shows the concentration ranges of the metal additions in this investigation. While previous work had shown that metals can decrease IP, there was effort to investigate a cause/effect relationship at different metal concentrations. Thus, different concentrations were screened. Biodiesel from soybean and cottonseed feed stocks were test to determine relative sensitivity to metal additions.

The data generated for each metal and feedstock are displayed in graphs 9 thru 24. The concentration ranges are given in Table 2 above. The blanks are included in the

graphs and are given at 0 ppm concentration. Every metal investigated had the ability to catalyze free radical oxidation and decrease IP. All graphs show that the effects of metal additions are nonlinear. The graphs “leveling-off” at higher concentrations as increasing concentrations have less ability to decrease the IP.

Collected Data

Data for Vanadium additions to soybean biodiesel

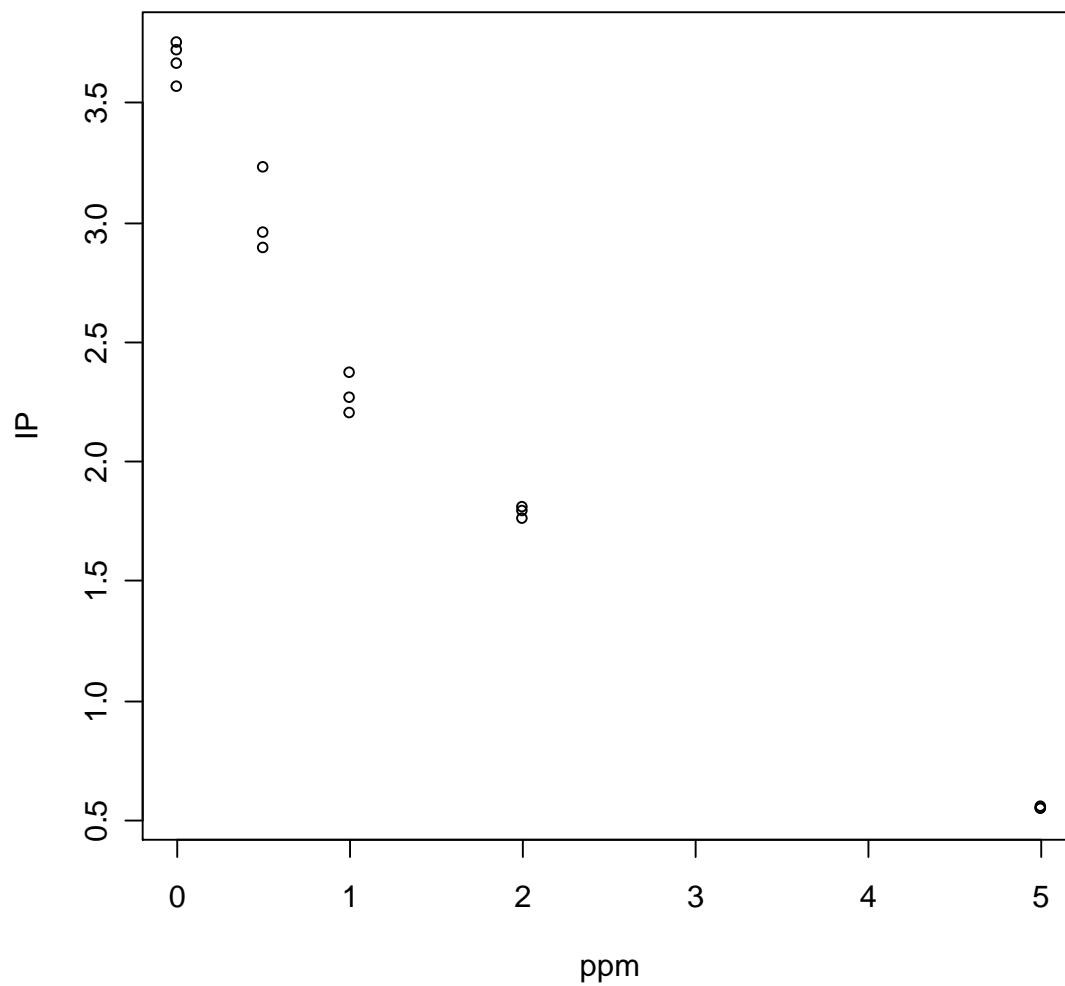


Figure 9
Data for additions of Vanadium to soybean biodiesel

Concentration range: 0.5 – 5.0 ppm

Maximum IP: 3.75 hrs - blank

Minimum IP: 0.55 hrs – 5.0 ppm V

Data for Vanadium additions to cottonseed biodiesel

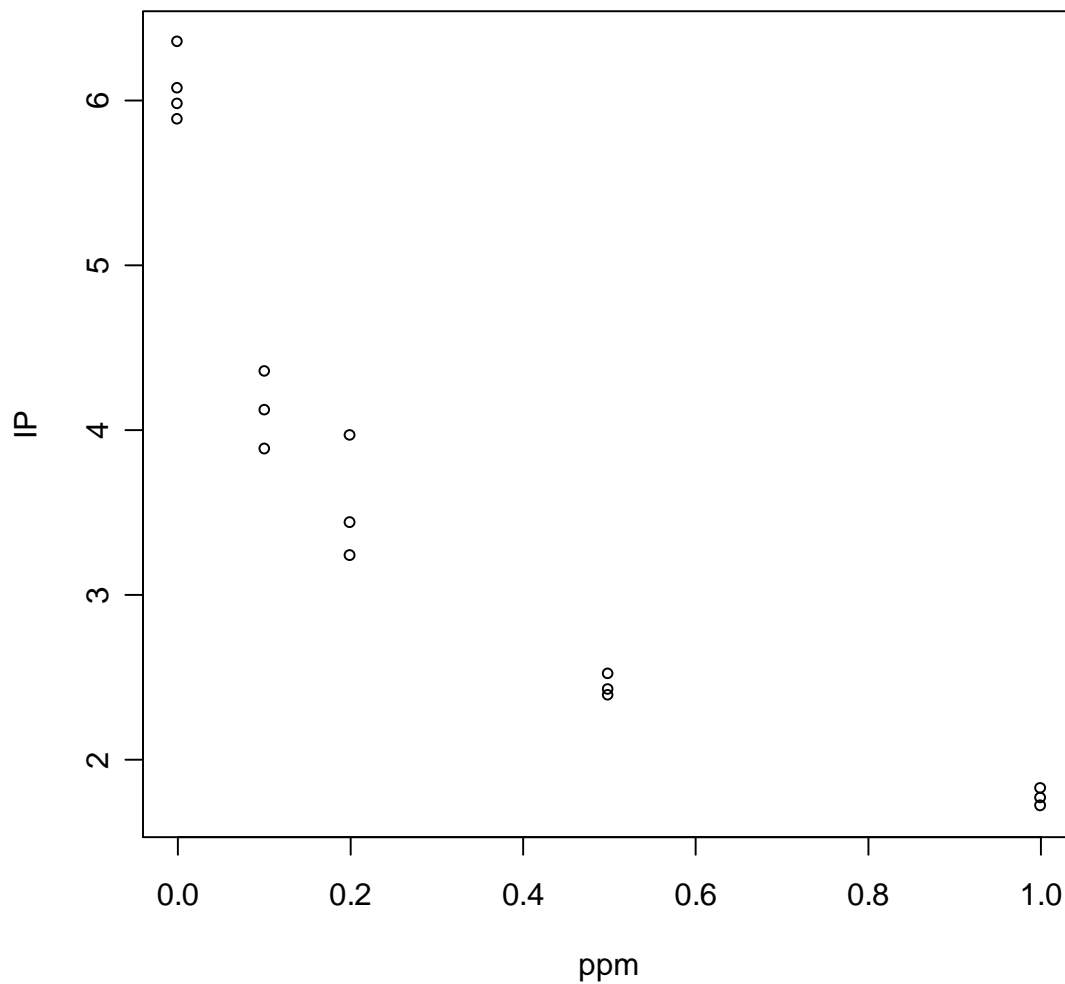


Figure 10

Data for additions of Vanadium to cottonseed biodiesel

Concentration range: 0.1 – 1.0 ppm

Maximum IP: 6.35 hrs - blank

Minimum IP: 1.72 hrs – 5.0 ppm V

Data for Chromium additions to soybean biodiesel

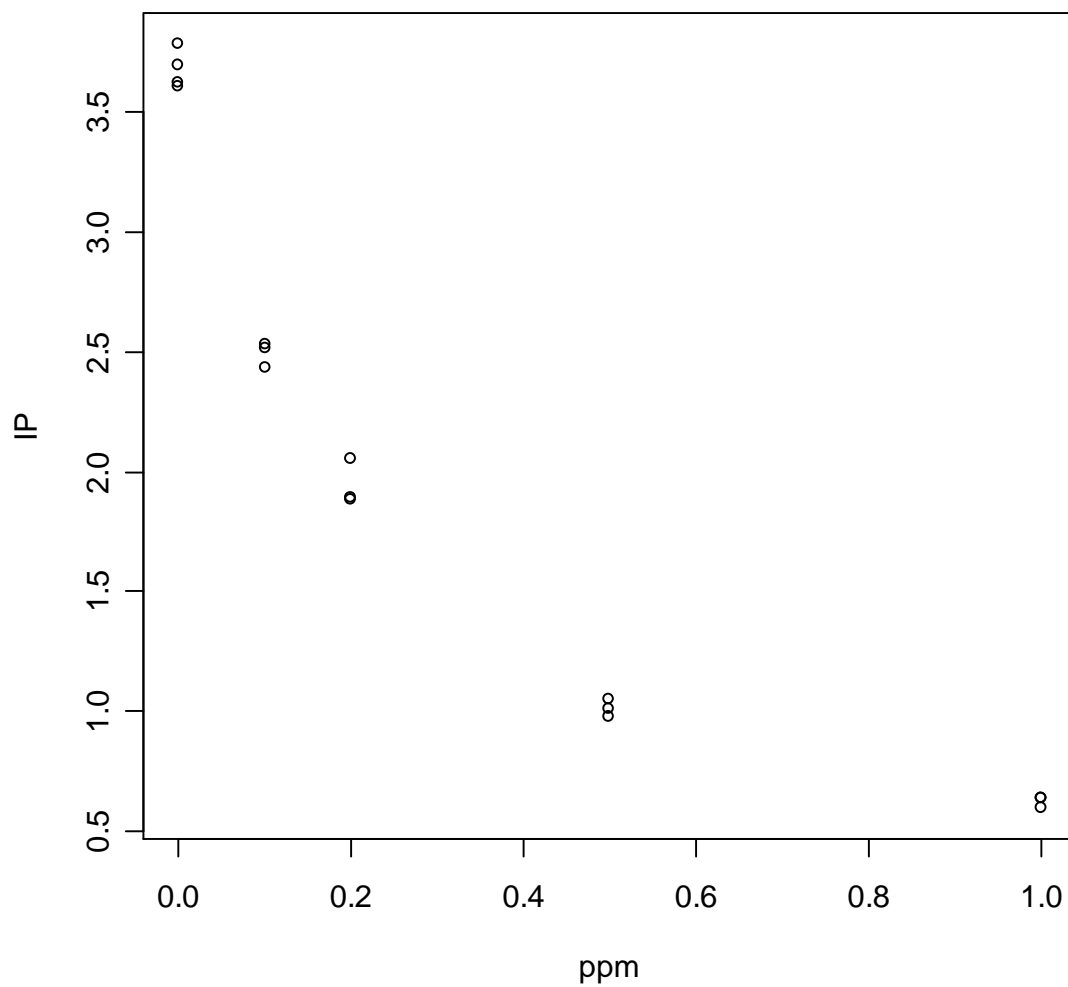


Figure 11

Data for additions of Chromium to soybean biodiesel

Concentration range: 0.1 – 1.0 ppm

Maximum IP: 3.78 hrs - blank

Minimum IP: 0.6 hrs – 1.0 ppm Cr

Data for Chromium additions to cottonseed biodiesel

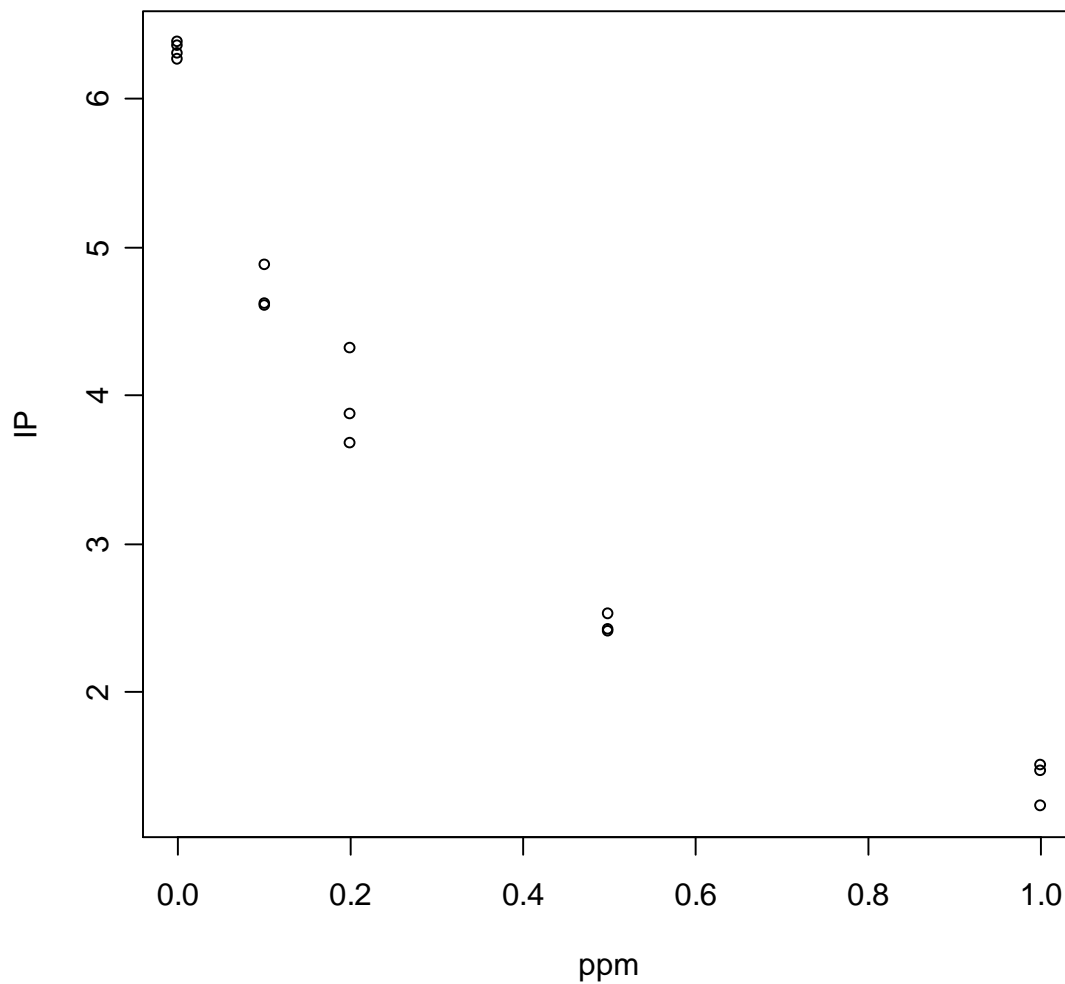


Figure 12

Data for additions of Chromium to cottonseed biodiesel

Concentration range: 0.1 – 1.0 ppm

Maximum IP: 6.38 hrs - blank

Minimum IP: 0.6 hrs – 1.23 ppm Cr

Data for Manganese in soybean biodiesel

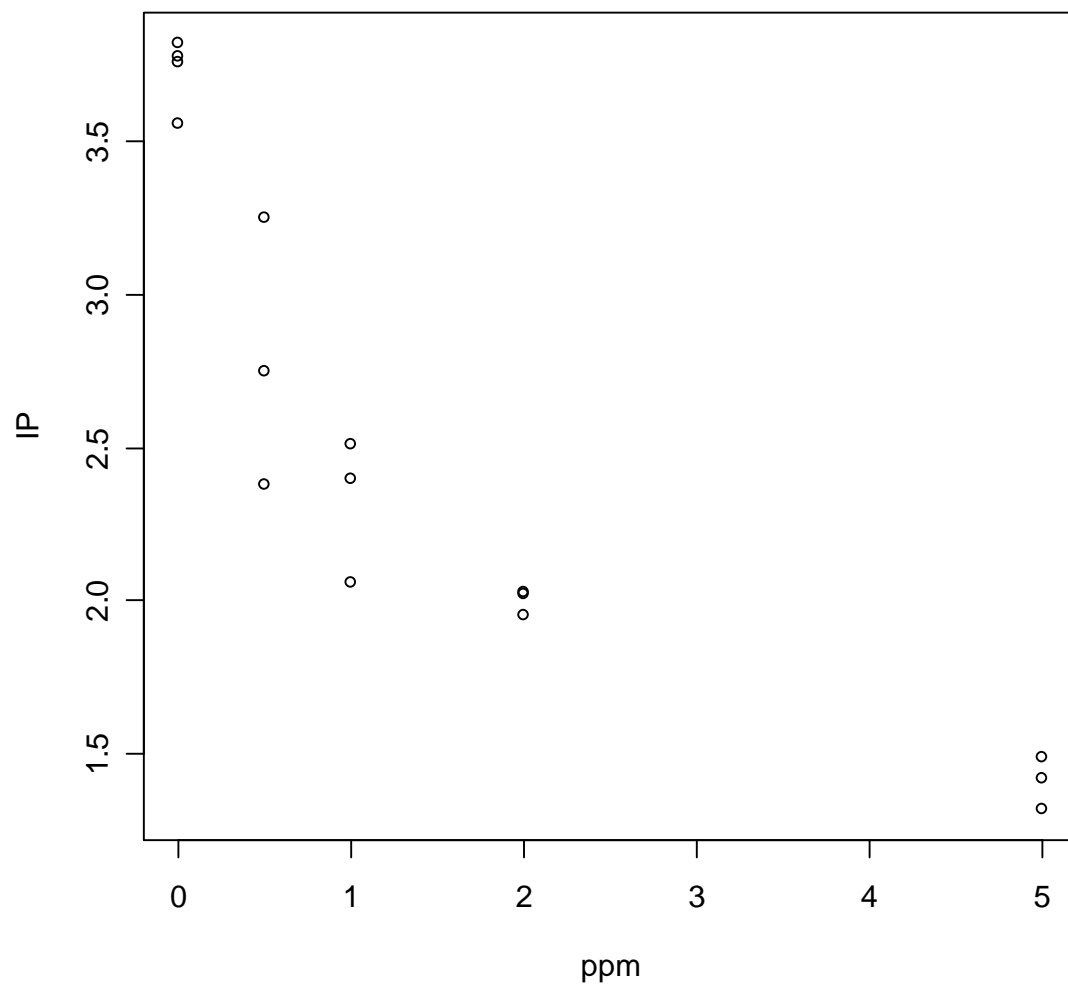


Figure 13

Data for additions of Manganese to soybean biodiesel

Concentration range: 0.5 – 5.0 ppm

Maximum IP: 3.82 hrs - blank

Minimum IP: 1.32 hrs – 5.0 ppm Mn

Data for Manganese additions to cottonseed biodiesel

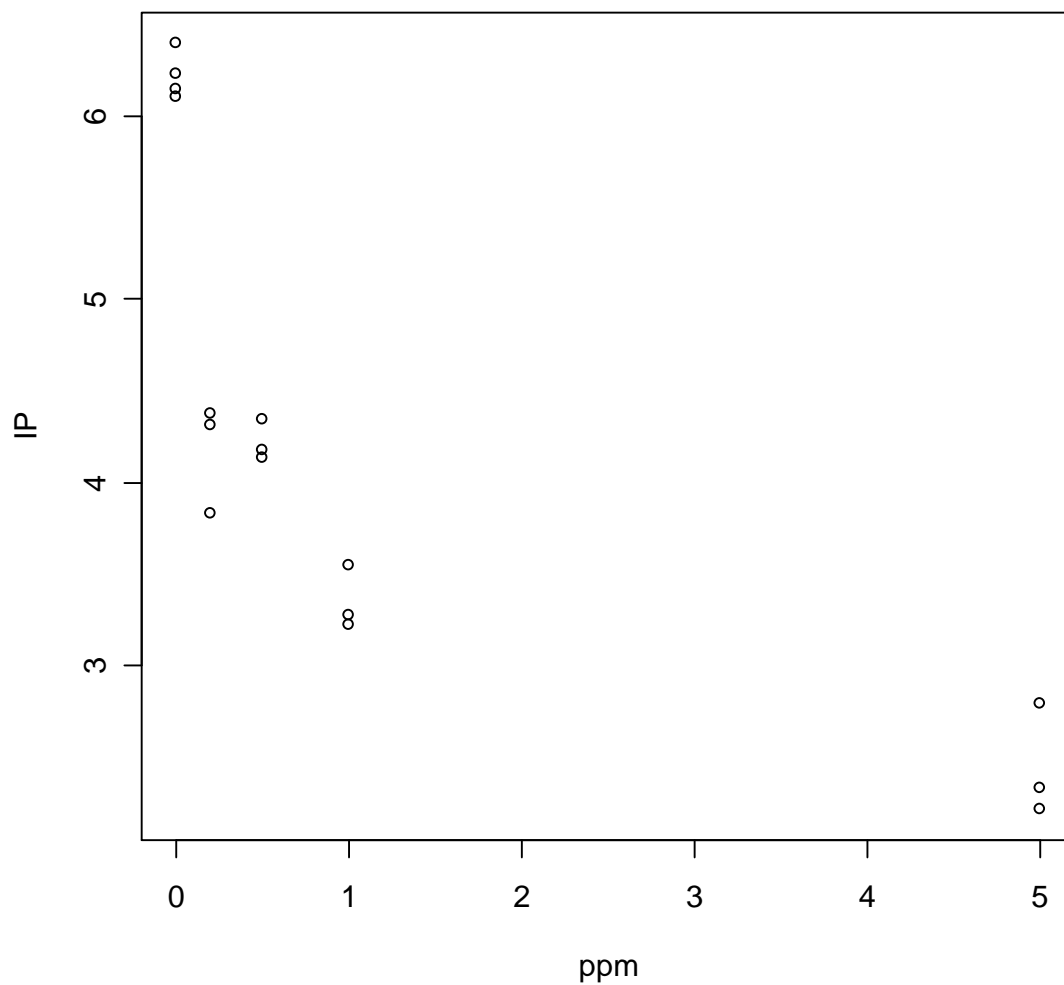


Figure 14

Data for additions of Manganese to cottonseed biodiesel

Concentration range: 0.2 – 5.0 ppm

Maximum IP: 6.40 hrs - blank

Minimum IP: 2.21 hrs – 5.0 ppm Mn

Data for Iron additions to soybean biodiesel

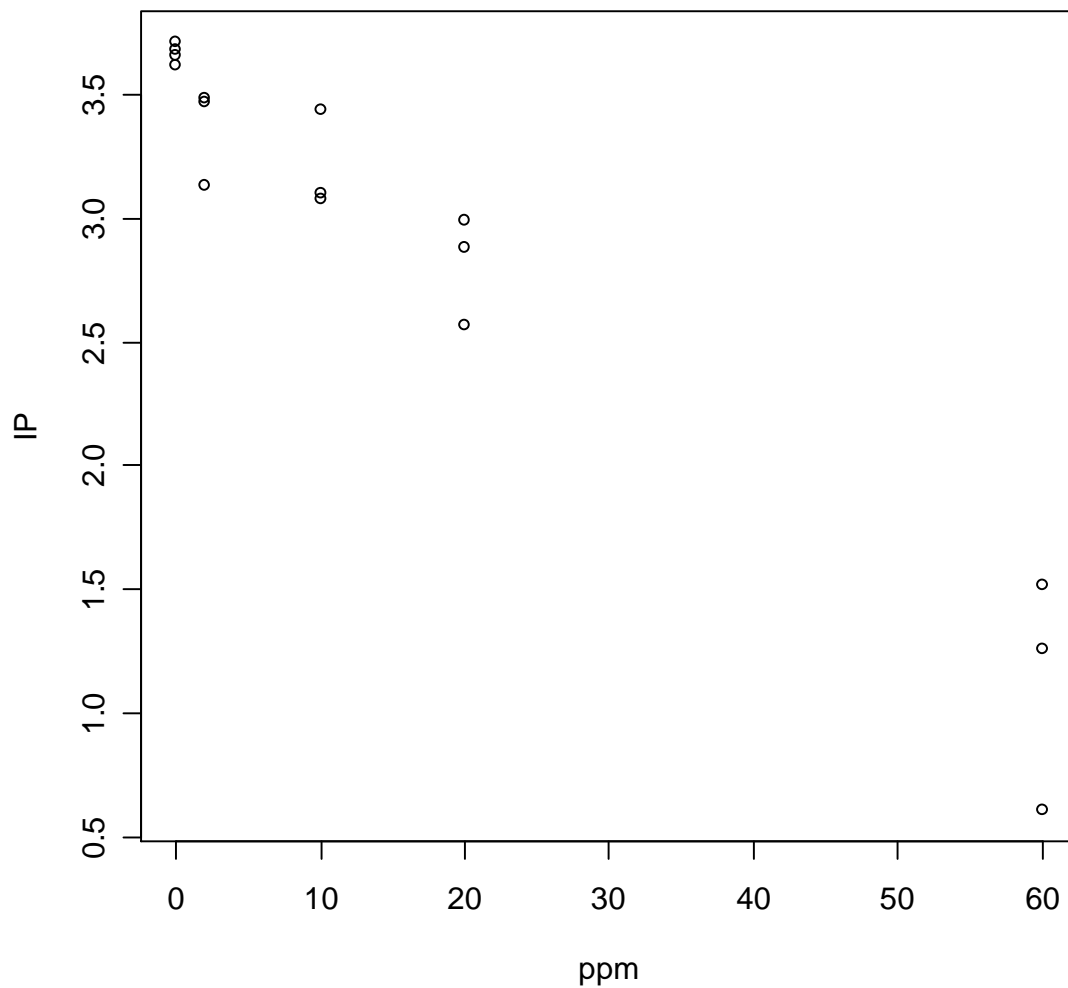


Figure 15

Data for additions of Iron to soybean biodiesel

Concentration range: 2 – 60 ppm

Maximum IP: 3.71 hrs - blank

Minimum IP: 0.61 hrs – 60 ppm Fe

Data for Iron additions to cottonseed biodiesel

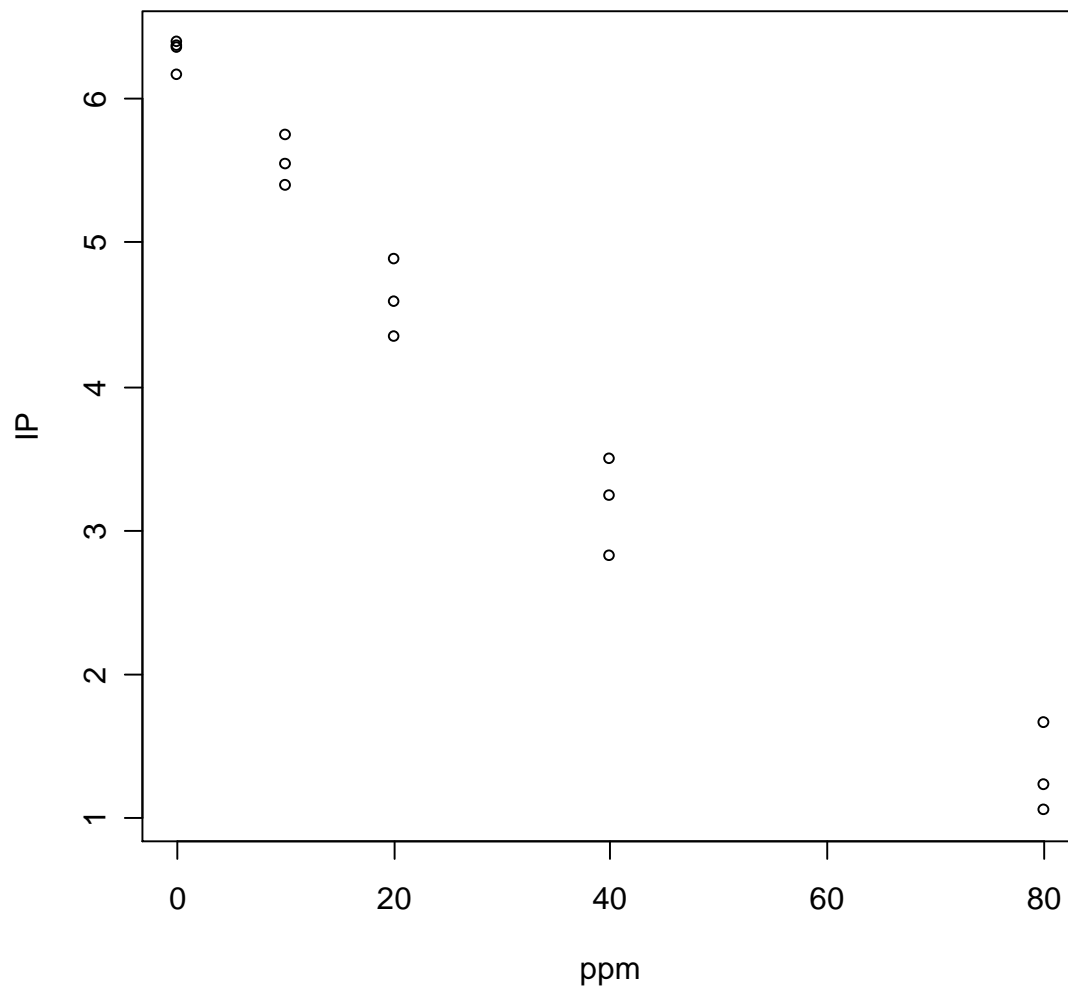


Figure 16

Data for additions of Iron to cottonseed biodiesel

Concentration range: 10 – 80 ppm

Maximum IP: 6.39 hrs - blank

Minimum IP: 1.06 hrs – 80 ppm Fe

Data for additions of Cobalt to soybean biodiesel

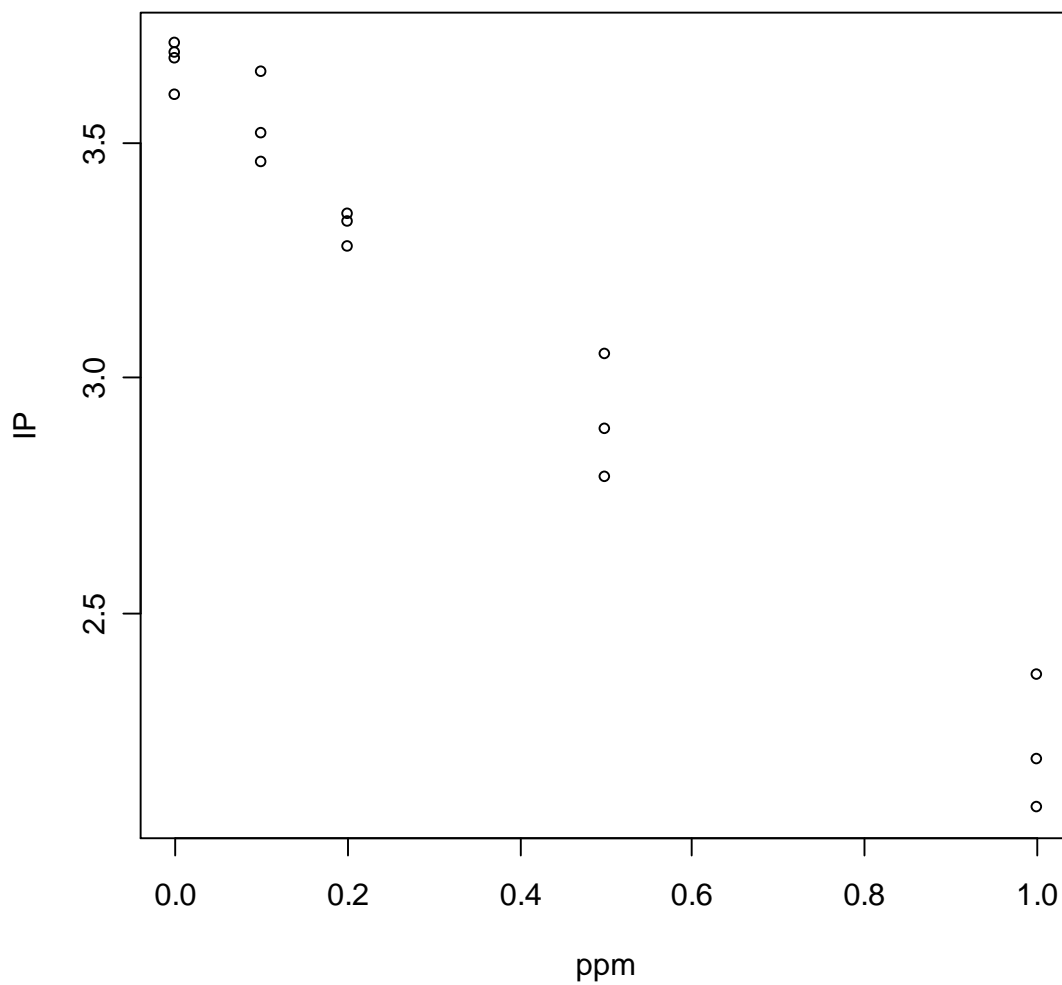


Figure 17

Data for additions of Cobalt to soybean biodiesel

Concentration range: 0.1 – 1.0 ppm

Maximum IP: 3.71 hrs - blank

Minimum IP: 2.09 hrs – 1.0 ppm Co

Data for additions of Cobalt to cottonseed biodiesel

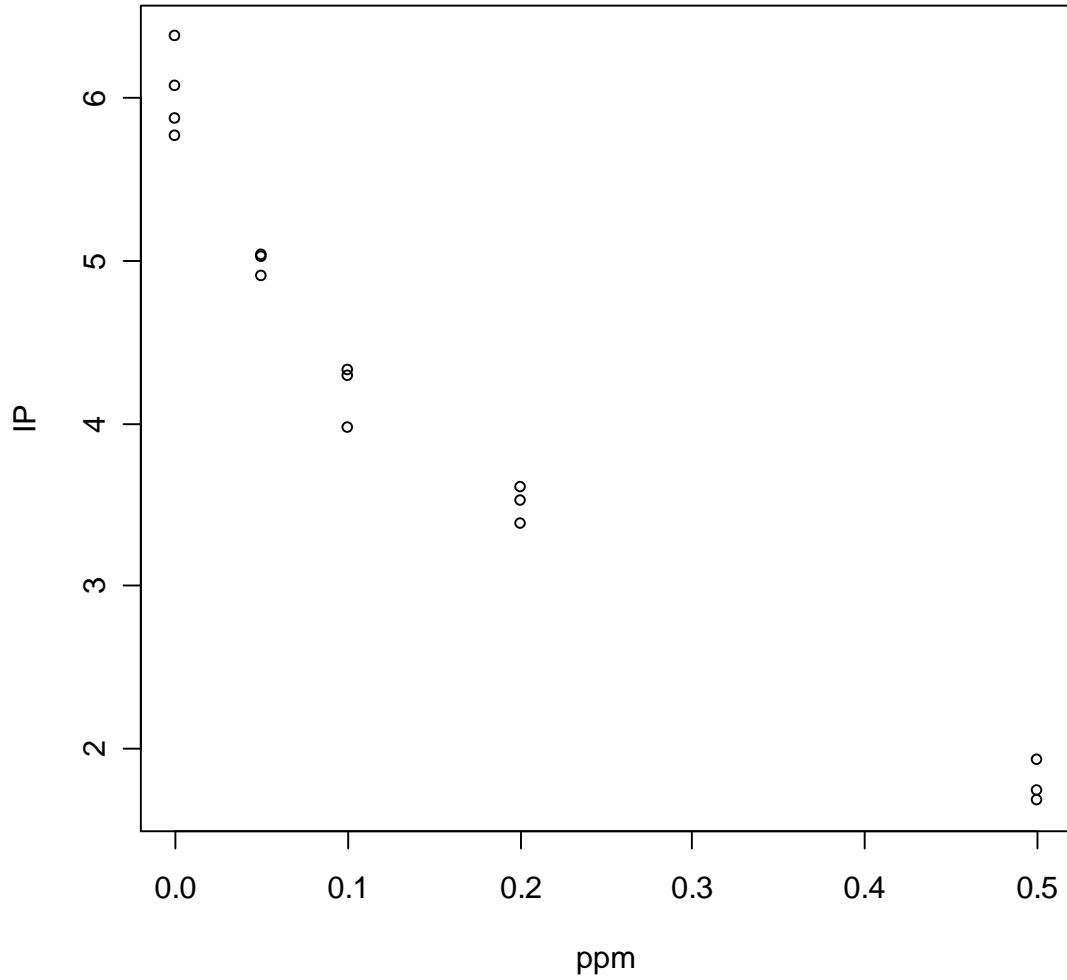


Figure 18

Data for additions of Cobalt to cottonseed biodiesel

Concentration range: 0.05 – 0.5 ppm

Maximum IP: 6.38 hrs - blank

Minimum IP: 1.68 hrs – 1.0 ppm Co

Data for additions of Nickel to soybean biodiesel

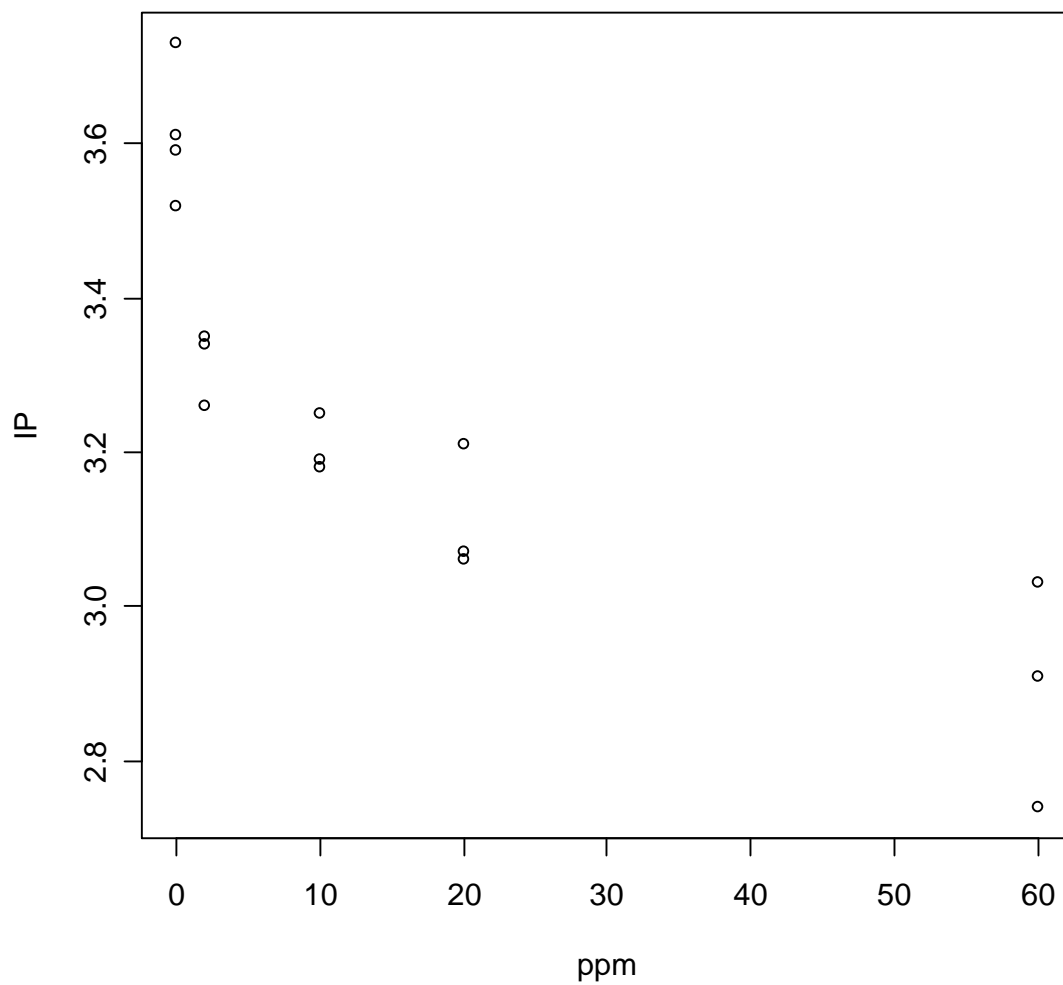


Figure 19

Data for additions of Nickel to soybean biodiesel

Concentration range: 2 – 60 ppm

Maximum IP: 3.73 hrs - blank

Minimum IP: 2.74 hrs – 60 ppm Ni

Data for additions of Nickel to cottonseed biodiesel

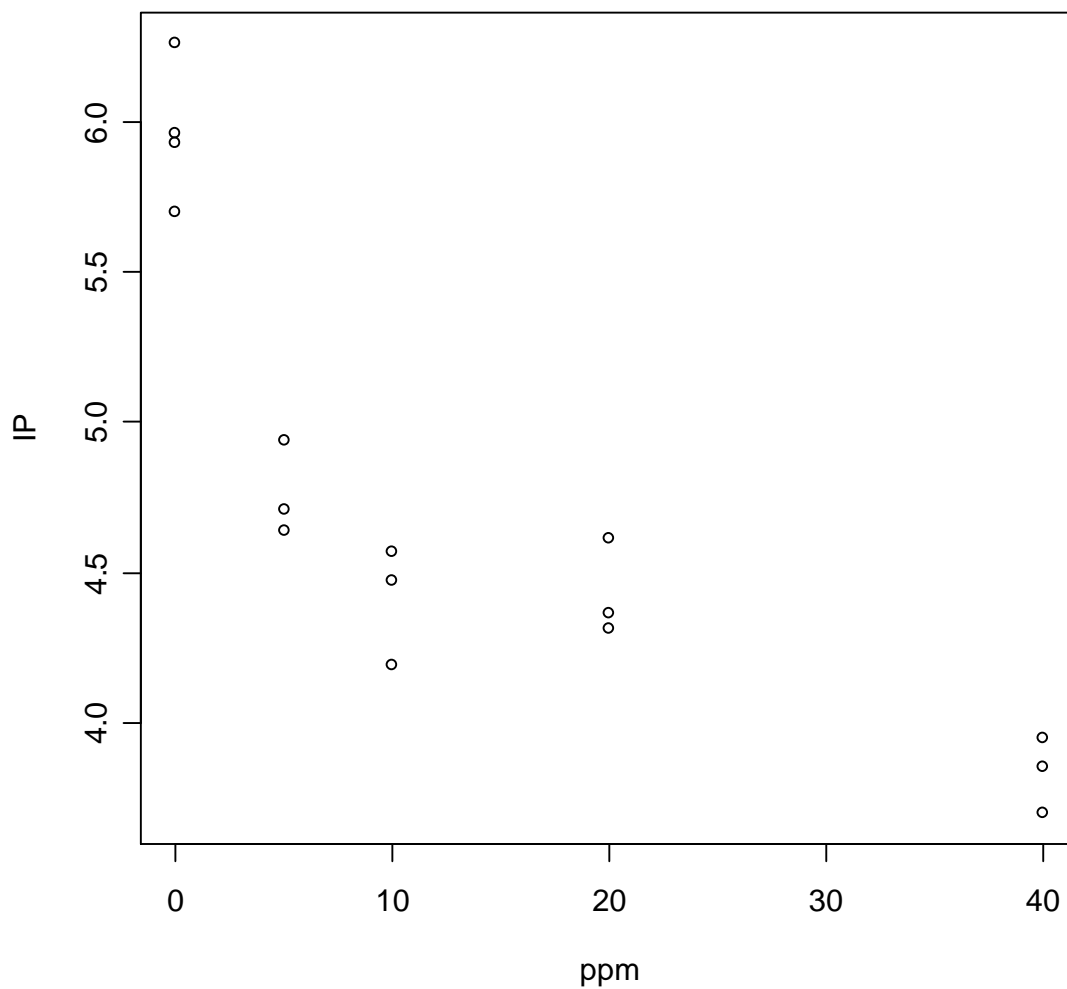


Figure 20

Data for additions of Nickel to cottonseed biodiesel

Concentration range: 5 – 40 ppm

Maximum IP: 6.26 hrs - blank

Minimum IP: 3.7 hrs – 40 ppm Ni

Data for additions of Copper to soybean biodiesel

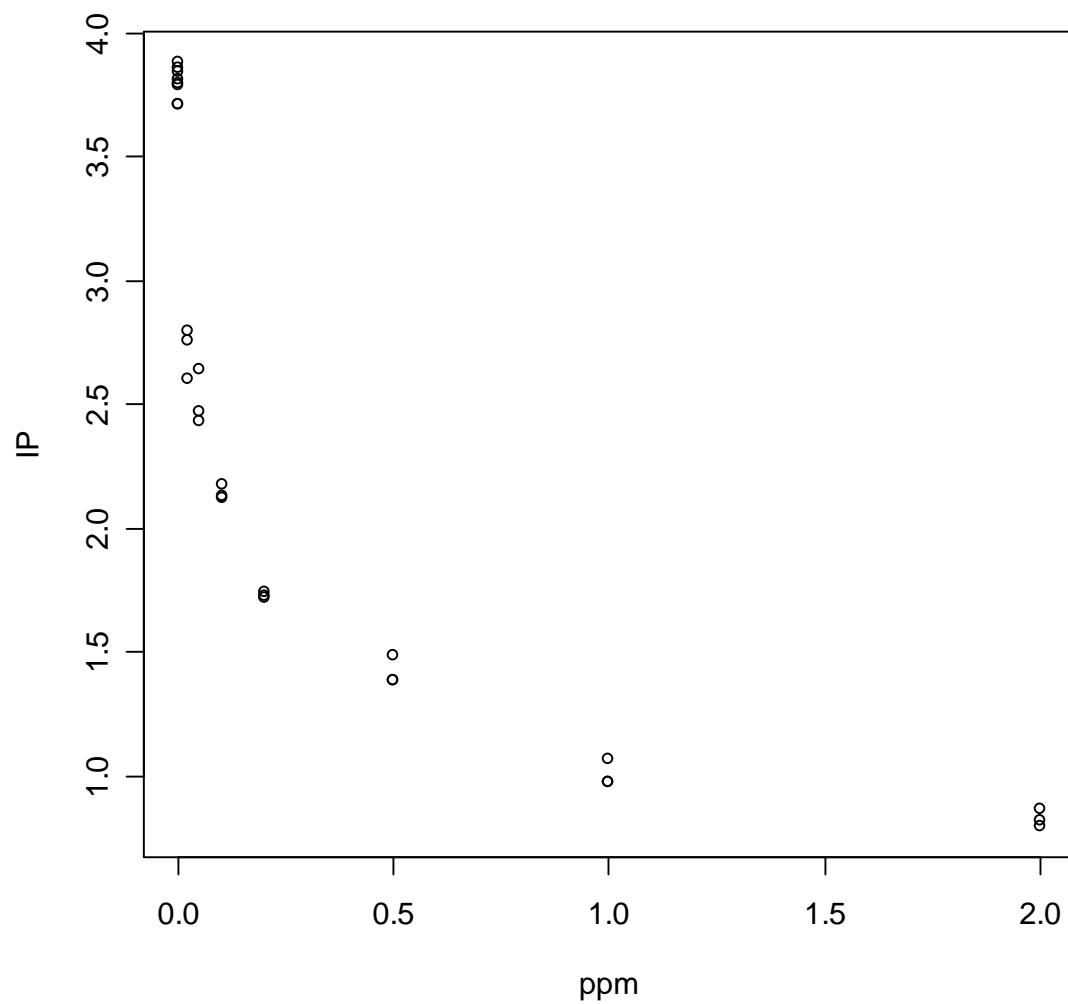


Figure 21

Data for additions of Copper to soybean biodiesel

Concentration range: 0.02 – 2.0 ppm

Maximum IP: 3.88 hrs - blank

Minimum IP: 0.8 hrs – 2.0 ppm Cu

Data for additions of Copper to cottonseed biodiesel

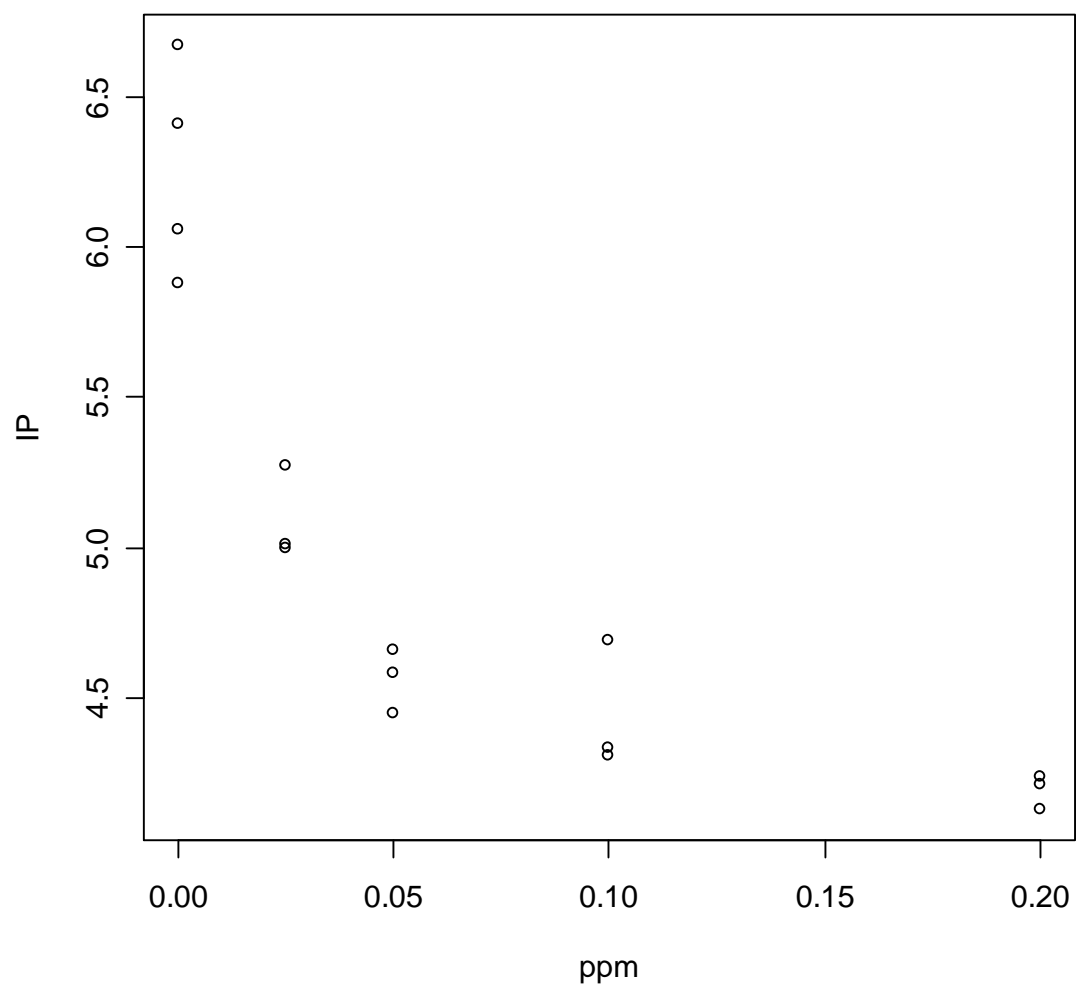


Figure 22

Data for additions of Copper to cottonseed biodiesel

Concentration range: 0.025 – 0.2 ppm

Maximum IP: 6.67 hrs - blank

Minimum IP: 4.13 hrs – 0.2 ppm Cu

Data for additions of Zinc to soybean biodiesel

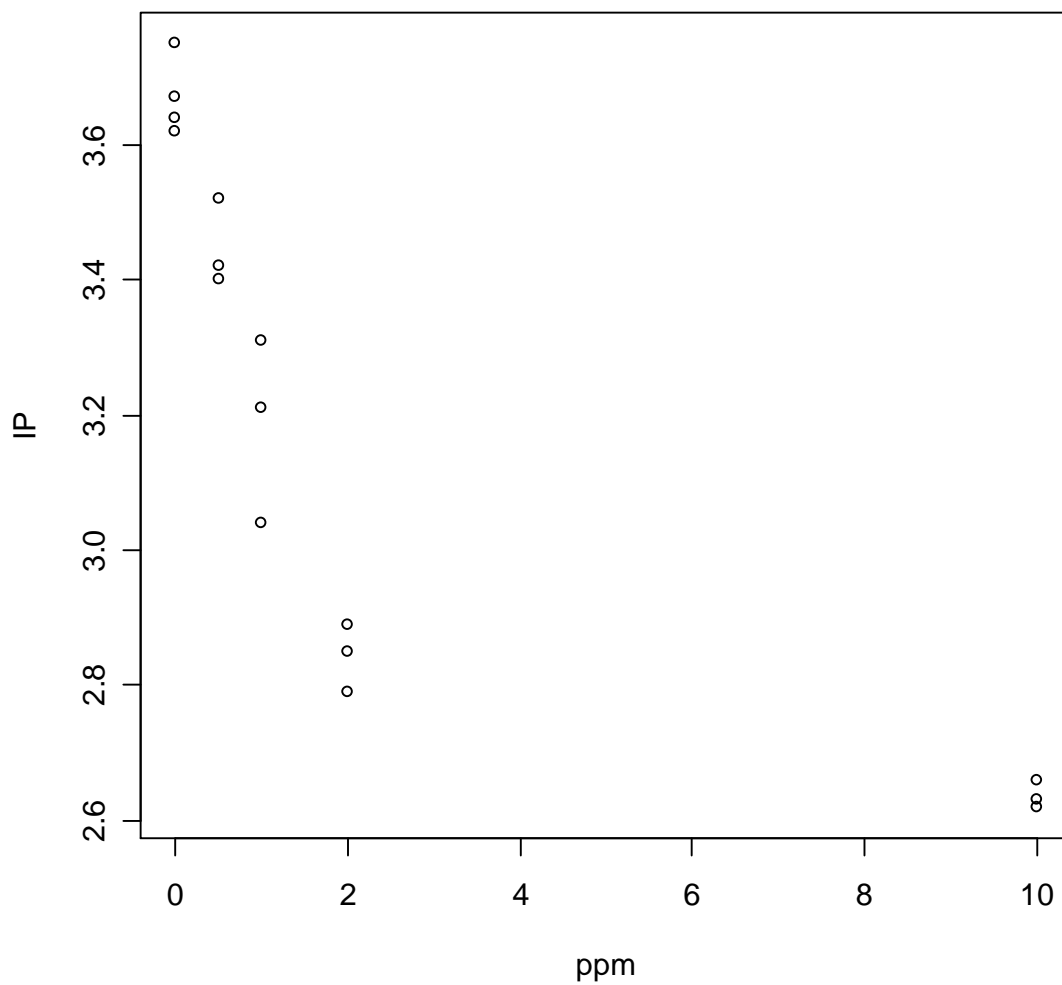


Figure 23

Data for additions of Zinc to soybean biodiesel

Concentration range: 0.5 – 10.0 ppm

Maximum IP: 3.67 hrs - blank

Minimum IP: 2.62 hrs – 10.0 ppm Zn

Data for Zinc additions to cottonseed biodiesel

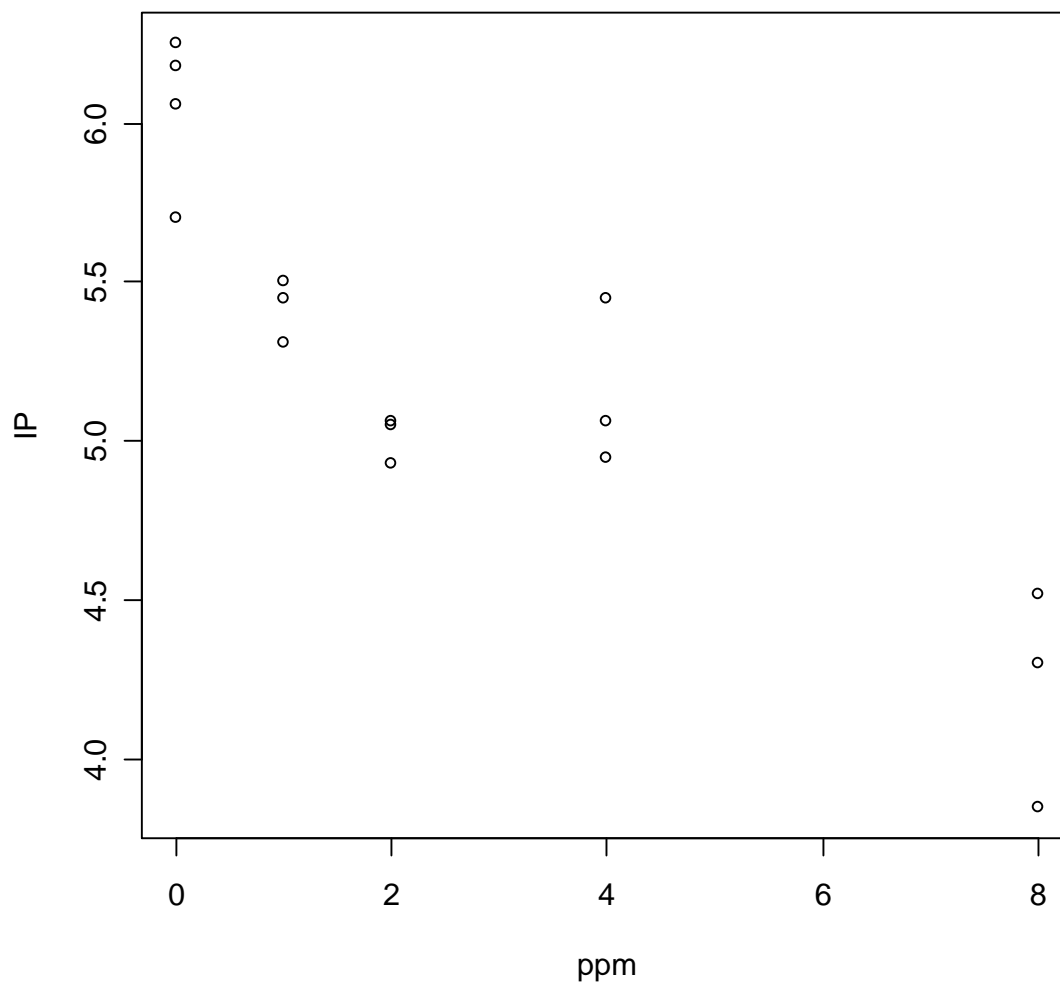


Figure 24

Data for additions of zinc to cottonseed biodiesel

Concentration range: 1.0 – 8.0 ppm

Maximum IP: 6.25 hrs - blank

Minimum IP: 3.85 hrs – 8.0 ppm Zn

Trends in data

The most active metal was copper which can decrease the IP at a concentration of 0.02 ppm in soybean biodiesel and 0.025 ppm in cottonseed biodiesel. The least active were iron and nickel which can decrease IP at 2 ppm in soybean biodiesel and 5 ppm in cottonseed biodiesel. Zinc is somewhat more active than iron and nickel depressing the IP at 1 ppm. The remaining metals: V, Cr, Mn, and Co are all active at concentrations less than 0.5 ppm.

Chapter 5 Linear Models

Linear Models Applied to the Data

The general form equation contains three coefficients that must be determined. The preferred method for determining such coefficients is regression analysis.[50] Since one explanatory variable is the square of another, the specific form of the analysis will be polynomial regression. This is one example of multiple regression modeling. With the proper choice of explanatory variables, a multiple regression model can describe a wide variety of phenomena. It is not necessary to make assumptions about the distribution of the explanatory variables.[51] This is important because the Rancimat is an “indirect” method of determining induction period that measures the rate of accumulation of oxidation breakdown products, not oxidation itself. Some criticize multiple regression as an example of “data dredging”.[51] However, the reader is reminded that the general form equation is a direct result of published work on the kinetics of fatty acid oxidation. Polynomial regression does require that there is no linear relation between explanatory variables. Since the $1/IP^2$ term and the $1/IP$ term are associated with separate and distinct free radical termination reactions, a linear relationship between them is not expected.

The linear model and the associated statistics are calculated with R, version 2.6.1.[52] A linear model for each metal/feedstock combination is calculated and the statistical significance of the coefficients is checked. Then the Pearson R-squared value is

checked. If it is less than 0.9 then the data is tested for outliers. Certain rules were applied for the selection of outliers described below. The metal additions were made in triplicate and blanks were run in duplicate. A Rancimat can hold eight samples. A fully loaded Rancimat contains two blanks and two groups of three metal samples for a total of eight. When searching for outliers it was decided to retain at least two out of triplicate metal samples (i.e. that it is forbidden for two out of three samples for a particular metal concentration to be classified outliers). The linear model is then recalculated without outliers.

R calculates several statistics with the determined linear model. A summary of the distribution of the residuals is given. Ideally, the median residual should be close to zero and the minimum is approximately the negative of the maximum. There are three statistics given with each estimated coefficient. These are the standard error, t test and p-value. The p-value for each coefficient should be less than 0.05 (i.e. 95% significance). The statistics for the linear model are the residual standard error, the degrees of freedom, the Adjusted R-squared correlation coefficient, the F-statistic and the associated p-value.

Outliers are the result of experimental errors. In the Rancimat there are two major groups of errors: those caused by inadequate cleaning and those caused by air flow leaks. Inadequate cleaning of the conductivity cell, reaction vessel cap or transfer hose reduces the induction period by introducing oxidation products. Leaks in reaction vessel cap or transfer hose increase the induction period. (See figure 7.) These errors result in outliers.

Residuals form the basis of the diagnostics tools used to identify outliers.[53, 54] R can generate four graphs based on residuals: 1) residuals vs. fitted values, 2) standardized residuals vs. theoretical quantiles, 3) the square root of the standardized residuals vs. fitted values and 4) the Cook's distance vs. observation number. The Cook's distance measures the influence of each observation on the regression coefficients.[51]

Models and Statistics

The results of the linear model, curve fitting and statistics for each metal and feedstock are given in Tables 5 through 20.

Linear models with statistics for Vanadium in soybean and cottonseed biodiesel

Min	1Q	Median	3Q	Max
-0.17689	-0.06097	-0.02665	0.04754	0.24102
Coefficients:	Estimate	Std. Error	t value	Pr(> t)
k ₀	-1.0117	0.5839	-1.733	0.114
k ₁	2.5865	3.0034	0.861	0.409
k ₂	4.9026	3.6105	1.358	0.204
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 2 and 10 DF	p-value
0.1143	10	0.9784	273.1	1.880e-09

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 5

Residuals, Coefficients, and statistics for Vanadium additions to soybean biodiesel

Data points for 5 ppm eliminated due to low IP

Residuals:

Min	1Q	Median	3Q	Max
-0.059752	-0.016328	-0.002303	0.007573	0.070056
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-0.13006	0.06867	-1.894	0.080680 .
k ₁	0.27190	0.42830	0.635	0.536545
k ₂	3.05227	0.58010	5.262	0.000154 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.03876	13	0.9892	684.9	6.697e-14

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 6

Residuals, Coefficients, and statistics for Vanadium additions to cottonseed biodiesel

Linear models and statistics for Chromium in soybean and cottonseed biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-0.015938	-0.006965	-0.002136	0.003809	0.024834
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-0.25597	0.02912	-8.789	1.04e-05 ***
k ₁	1.00048	0.10688	9.361	6.18e-06 ***
k ₂	-0.23913	0.08088	-2.957	0.0160 *
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 1 and 14 DF	p-value
0.01383	9	0.995	1094	1.801e-11

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 7

Residuals, Coefficients, and statistics for Chromium additions to soybean biodiesel

Data points for 1 ppm eliminated due to low IP

Residuals:

Min	1Q	Median	3Q	Max
-0.076887	-0.026423	0.001722	0.018720	0.084076
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-0.43355	0.05301	-8.178	1.76e-06 ***
k ₁	2.82784	0.29668	9.532	3.13e-07 ***
k ₂	-1.19311	0.32250	-3.700	0.00267 **
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 13	p-value
0.04454	13	0.9876	517.2	4.071e-13

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 8

Residuals, Coefficients, and statistics for Chromium additions to cottonseed biodiesel

Linear models and statistics for Manganese in soybean and cottonseed biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-0.69137	-0.05893	0.02401	0.20976	0.81300
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-0.2988	0.9929	-0.301	0.7683
k ₁	-2.6553	4.3553	-0.610	0.5526
k ₂	13.9152	4.3821	3.175	0.0073 **
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 1 and 14 DF	p-value
0.4093	13	0.9499	143.1	1.405e-09

Signif. codes: 0 '****' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 9

Residuals, Coefficients, and statistics for Manganese additions to soybean biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-0.690080	-0.282975	-0.001742	0.115244	2.252957
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	0.8643	1.7795	0.486	0.6353
k ₁	-15.3691	12.8336	-1.198	0.2525
k ₂	57.5354	21.4137	2.687	0.0187 *
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 12 DF	p-value
0.7202	13	0.8549	45.19	1.402e-06

Signif. codes: 0 '****' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 10

Residuals, Coefficients, and statistics for Manganese additions to cottonseed biodiesel

Linear models and statistics for Iron in soybean and cottonseed biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-8.7279	-1.5883	-0.7889	0.9702	6.4036
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-120.43	92.45	-1.303	0.222
k ₁	619.48	579.52	1.069	0.310
k ₂	-654.08	898.59	-0.728	0.483
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 13 DF	p-value
4.255	10	0.7295	17.18	0.000582

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 11

Residuals, Coefficients, and statistics for Iron additions to soybean biodiesel

Data for 60 ppm removed

Residuals:

Min	1Q	Median	3Q	Max
-5.0853	-1.3669	0.2144	1.2163	3.4819
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-92.9	13.5	-6.883	7.2e-05 ***
k ₁	760.0	116.2	6.541	0.000106 ***
k ₂	-1076.1	233.1	-4.617	0.001259 **
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 13 DF	p-value
2.676	9	0.97	178.7	5.703e-08

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 12

Residuals, Coefficients, and statistics for Iron additions to cottonseed biodiesel

Linear models and statistics for Cobalt in soybean and cottonseed biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-0.092993	-0.037983	-0.002295	0.010377	0.113095
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-3.3104	0.5583	-5.929	4.99e-05 ***
k ₁	16.2109	3.1657	5.121	0.000196 ***
k ₂	-14.8439	4.3057	-3.448	0.004329 **
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 13 DF	p-value
0.05976	13	0.9776	284.3	1.864e-11

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 13

Residuals, Coefficients, and statistics for Cobalt additions to soybean biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-0.039150	-0.006875	-0.003473	0.010514	0.035361
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-0.34949	0.04007	-8.722	8.58e-07 ***
k ₁	2.29279	0.25934	8.841	7.37e-07 ***
k ₂	-1.40094	0.34109	-4.107	0.00124 **
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 13 DF	p-value
0.01902	13	0.9906	686.2	6.613e-14

Signif. Codes : '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 14

Residuals, Coefficients, and statistics for Cobalt additions to cottonseed biodiesel

Linear models and statistics for Nickel in soybean and cottonseed biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-12.049	-6.407	-3.199	2.857	29.712
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	428.9	349.1	1.229	0.2410
k ₁	-3381.2	2234.4	-1.513	0.1541
k ₂	6585.3	3560.9	1.849	0.0873 .
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 11 DF	p-value
11.2	13	0.7508	23.6	4.713e-05

Signif. Codes : '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 15

Residuals, Coefficients, and statistics for Nickel additions to soybean biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-11.49437	-3.30030	0.03103	2.70700	9.80017
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	121.41	57.28	2.120	0.05385 .
k ₁	-1450.72	548.06	-2.647	0.02013 *
k ₂	4324.48	1289.56	3.353	0.00519 **
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 11 DF	p-value
5.61	13	0.853	44.51	1.528e-06

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 16

Residuals, Coefficients, and statistics for Nickel additions to cottonseed biodiesel

Linear models and statistics for Copper in soybean and cottonseed biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-0.069139	-0.028998	-0.007766	0.016853	0.131075
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-0.03314	0.05979	-0.554	0.585
k ₁	-0.28729	0.22811	-1.259	0.221
k ₂	1.34017	0.18514	7.239	2.28e-07 ***
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 26 DF	p-value
0.05103	23	0.9759	506.6	< 2.2e-16

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 17

Residuals, Coefficients, and statistics for Copper additions to soybean biodiesel

Data for 2 ppm removed

Figure 38

Least squares curve fit for Copper additions to cottonseed biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-0.052399	-0.016800	0.003742	0.013235	0.044725
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	1.232	0.405	3.042	0.00945 **
k ₁	-14.342	4.191	-3.422	0.00455 **
k ₂	41.456	10.631	3.900	0.00183 **
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 11 DF	p-value
0.03011	13	0.8306	37.78	3.831e-06

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 18

Residuals, Coefficients, and statistics for Copper additions to cottonseed biodiesel

Linear models and statistics for Zinc in soybean and cottonseed biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-4.6115	-0.5904	0.2452	1.0150	2.3065
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	112.32	39.56	2.839	0.01394 *
k ₁	-758.00	246.44	-3.076	0.00885 **
k ₂	1275.97	378.22	3.374	0.00499 **
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 2 and 12 DF	p-value
1.704	13	0.7957	30.2	1.298e-05

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 19

Residuals, Coefficients, and statistics for Zinc additions to soybean biodiesel

Residuals:

Min	1Q	Median	3Q	Max
-1.6941	-1.1562	-0.2076	0.7196	2.4968
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k ₀	-19.09	17.03	-1.121	0.283
k ₁	125.16	167.06	0.749	0.467
k ₂	125.16	404.30	-0.156	0.878
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 1 and 10 DF	p-value
1.391	13	0.7739	26.67	2.506e-05

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 20

Residuals, Coefficients, and statistics for Zinc additions to cottonseed biodiesel

Summary of results using Equation 6

Equation 6 was derived above relating metal ion concentration to induction period (IP):

$$[M] = \frac{k_2}{IP^2} + \frac{k_1}{IP} + k_0$$

Equation 6

In this equation the signs of k_0 , k_1 , and k_2 are not arbitrary. The coefficient k_0 , which comes from the constant of integration, should be negative. The biodiesel samples received will not be perfectly pure. Some catalytic metal contamination will be introduced during biodiesel synthesis and storage. The coefficient k_0 represents an amount of metallic contamination relative to the metal being tested. Because it adds to $[M]$, the coefficient k_0 must be negative on the right side of the equation (i.e. positive on the left side). The signs of k_1 and k_2 must be positive. These two coefficients are derived from the rate constants of free radical initiation, propagation, and termination and the molar concentrations of biodiesel, hydroperoxide, antioxidant, and free radicals. Since all these values are positive it follows that k_1 and k_2 must also be positive

Table 21 contains a summary of the results of a least squares fit of Equation 6 to the data collected for the eight metals and two feedstocks that were tested.

Metal.feedstock	k_0	k_1	k_2
V.soy	-1.0117	2.5865	4.9026
V.cotton	-0.13006	0.27190	3.05227
Cr.soy	-0.25597	1.00048	-0.23913
Cr.cotton	-0.43355	2.82784	-1.19311
Mn.soy	-0.2988	-2.6553	13.9152
Mn.cotton	0.8643	-15.3691	57.5354
Fe.soy	-120.43	619.48	-654.08
Fe.cotton	-92.9	760.0	-1076.1
Co.soy	-3.3104	16.2109	-14.8439
Co.cotton	-0.34949	2.29279	-1.40094
Ni.soy	428.9	-3381.2	6585.3
Ni.cotton	121.41	-1450.72	4324.48
Cu.soy	-0.03314	-0.28729	1.34017
Cu.cotton	1.232	-14.342	41.456
Zn.soy	112.32	-758.00	1275.97
Zn.cotton	-19.09	125.16	125.16

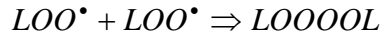
Table 21
Summary of coefficients for equation $[M] = k_2/IP^2 + k_1/IP + k_0$

The results summarized in Table 19 show that the results of using Equation 6 for the linear model are not good. The numbers highlighted in red have the wrong sign. Only the least squares fits for Vanadium have the correct signs. All other contain coefficients with incorrect signs.

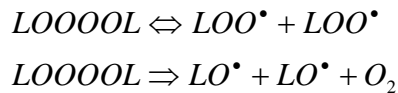
New Model with Curve Fit and Statistics

Is it possible to simplify the formula (i.e. to remove a term and the associated coefficient) and get better results? If so, what coefficient should be removed? Coefficient k_0 must be included since samples cannot be perfectly pure. Coefficient k_1 is associated with the alkoxy radical concentration which is reported to generate biodiesel oxidation

products. The coefficient k_2 is specific for the hydroperoxide to hydroperoxide termination reaction.



This reaction results in four atoms of oxygen bonded in sequence. If this termination reaction is not thermally stable then it will decompose back into free radicals before rearrangement of the four atoms of oxygen can produce biodiesel oxidation products.



Therefore, it was decided to remove the term (k_2 / IP^2) from Equation 6 to generate Equation 7 below.

$$[M] = \frac{k_1}{IP} + k_0$$

Equation 7

The simplification allows a rearrangement of Equations 7 which gives a simpler form:

$$\begin{aligned}
[M] &= \frac{k_1}{IP} + k_0 \\
[M] - k_0 &= \frac{k_1}{IP} \\
k_1([M] - k_0) &= \frac{1}{IP} \\
k'_1[M] - k'_0 &= \frac{1}{IP} \\
\frac{1}{IP} &= k'_1[M] - k'_0
\end{aligned}$$

The result is Equation 8. Recall that the sign of k_0 is required to be negative. Thus, it is more intuitive to change the sign to positive in the final equation. Coefficients k'_1 and k_1 are not distinguished.

$$\frac{1}{IP} = k_1[M] + k_0$$

Equation 8

A new set of curve fits and statistics for the eight metals and two biodiesel feedstocks were generated with a linear model base on Equation 8.

It was decided to eliminate high metal concentrations producing induction periods less than one hour from the data sets. Such short induction periods data points can be disproportionately influenced by errors. This decision resulted in the elimination of the 5 ppm addition of V to soybean biodiesel, the 1 ppm addition of Cr to soybean biodiesel, and the 2 ppm addition of Cu to soybean biodiesel. None of the additions to cottonseed biodiesel produced induction periods less than 1 hour. The 60 ppm addition of Fe to soybean biodiesel and the 80 ppm addition of Fe to cottonseed biodiesel were also

eliminated due to high large amounts of insoluble precipitates generated during the induction period test.

New linear model with curve fit and statistics for Vanadium in soybean biodiesel

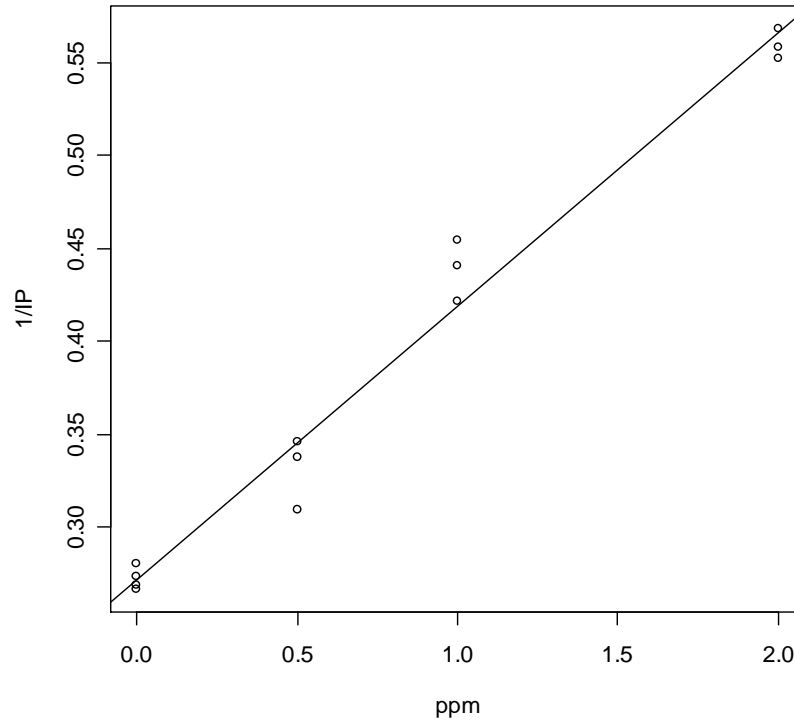


Figure 25
Least squares fit of Vanadium additions to soybean biodiesel

Min	1Q	Median	3Q	Max
-0.0357559	-0.0075156	0.0006673	0.0029596	0.0355641
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.271726	0.007209	37.69	5.54e-13 ***
k_1	0.147256	0.006550	22.48	1.52e-10 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.01766	11	0.9768	505.5	1.518e-10

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 22
Residuals, coefficients and statistics for Vanadium additions to soybean biodiesel

New linear model with curve fit and statistics for Vanadium in cottonseed biodiesel

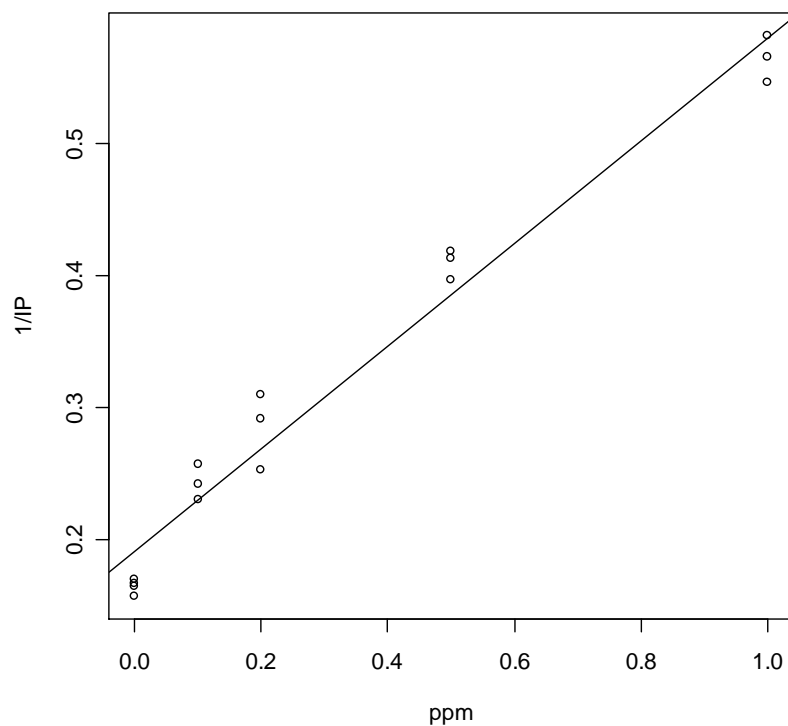


Figure 26
Least squares fit of Vanadium additions to cottonseed biodiesel

Min	1Q	Median	3Q	Max
-0.0341384	-0.0221917	0.0002167	0.0234435	0.0402316
Coefficients	Estimate	Std. Error	t value	Pr(> t)
k_0	0.191619	0.008931	21.46	4.14e-12 ***
k_1	0.388736	0.018090	21.49	4.05e-12 ***
Residual standard error	Degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.02607	14	0.9685	461.8	4.052e-12

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 23
Residuals, coefficients and statistics for Vanadium additions to cottonseed biodiesel

New linear model with curve fit and statistics for Chromium in soybean biodiesel

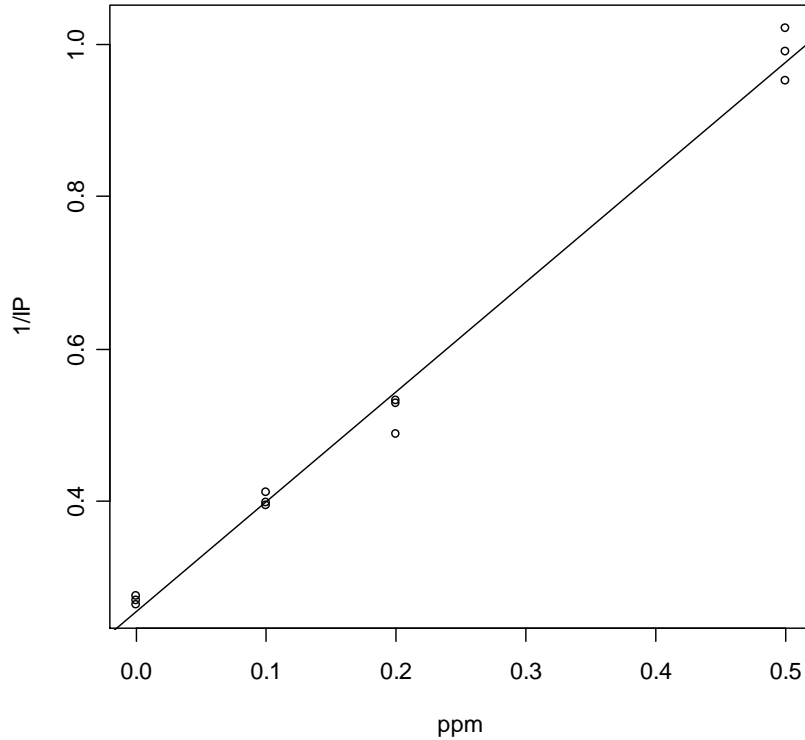


Figure 27

Least squares fit of Chromium additions to soybean biodiesel

Min	1Q	Median	3Q	Max
-0.056253	-0.012846	0.003845	0.013772	0.043502
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.25549	0.01127	22.66	6.30e-10***
k_1	1.44283	0.04116	35.05	8.47e-12***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 10 DF	p-value
0.02668	10	0.9911	1229	8.473e-12

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 24

Residuals, coefficients, and statistics for Chromium additions to soybean biodiesel

New linear model with curve fit and statistics for Chromium in cottonseed biodiesel

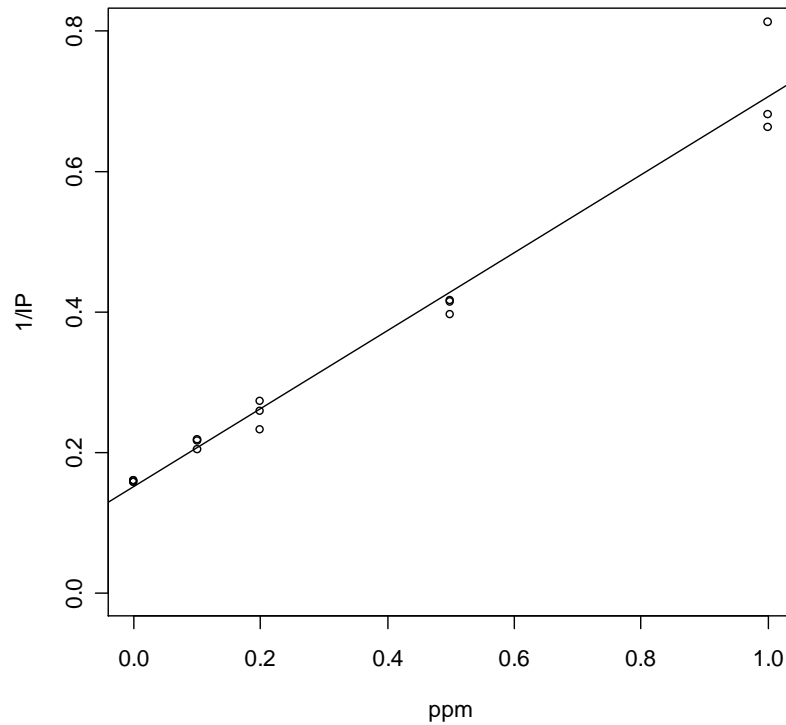


Figure 28

Least squares fit of Chromium additions to cottonseed biodiesel

Min	1Q	Median	3Q	Max
-0.045310	-0.018640	0.002571	0.009485	0.105447
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.15040	0.01189	12.65	4.73e-09 ***
k_1	0.55716	0.02408	23.14	1.48e-12 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.0347	14	0.9727	535.5	1.476e-12

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 25

Residuals, coefficients, and statistics for Chromium additions to cottonseed biodiesel

New linear model with curve fit and statistics for Manganese in soybean biodiesel

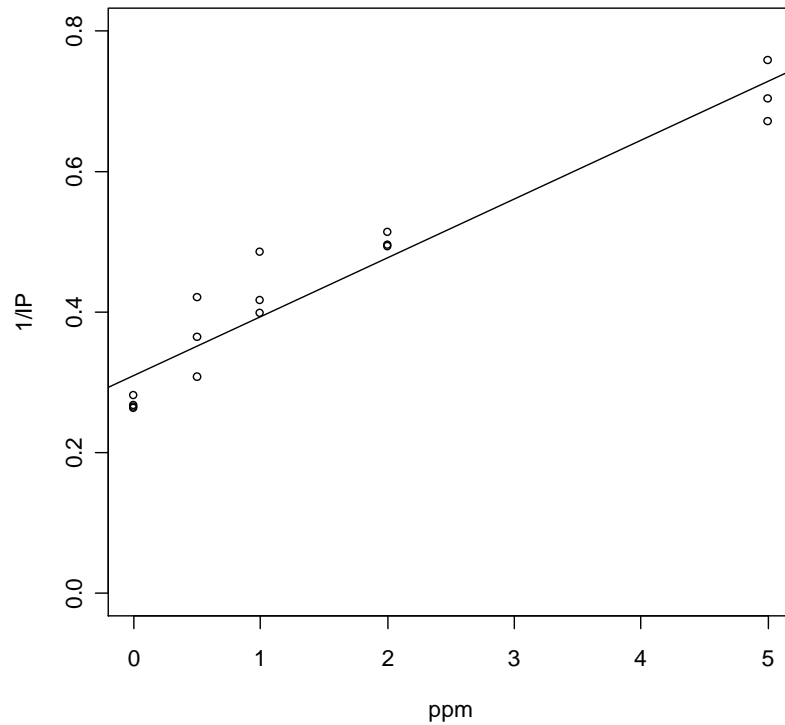


Figure 29

Least squares fit of Manganese additions to soybean biodiesel

Min	1Q	Median	3Q	Max
-0.057922	-0.044210	0.008053	0.024192	0.091522
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.310128	0.015423	20.11	9.99e-12 ***
k_1	0.083787	0.006476	12.94	3.54e-09 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.04584	14	0.9173	167.4	3.538e-09

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 26

Residuals, coefficients, and statistics for Manganese additions to soybean biodiesel

New linear model with curve fit and statistics for Manganese in cottonseed biodiesel

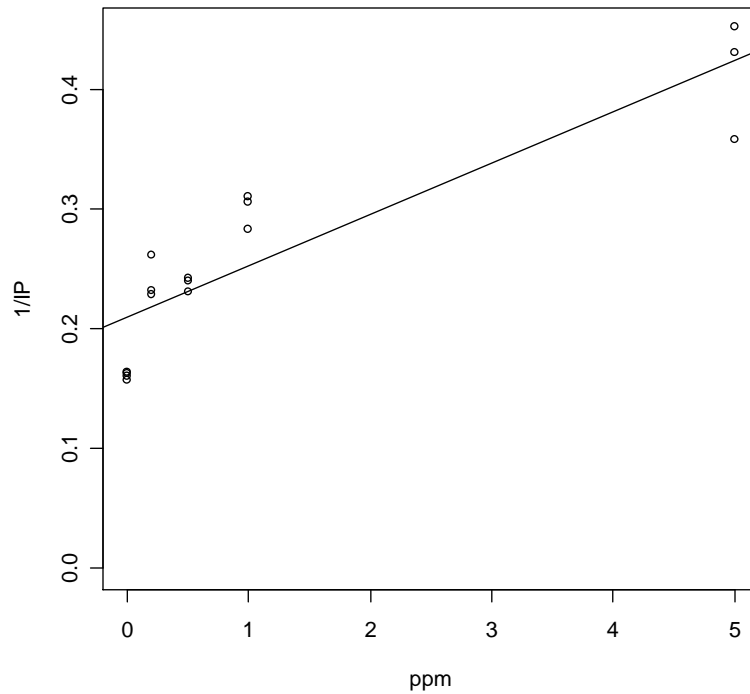


Figure 30

Least squares fit of Manganese additions to cottonseed biodiesel

Min	1Q	Median	3Q	Max
-0.066505	-0.046110	0.009732	0.028144	0.057966
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.209510	0.012606	16.620	1.30e-10 ***
k_1	0.043084	0.005678	7.588	2.52e-06 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.04157	14	0.7905	57.58	2.519e-06

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 27

Residuals, coefficients, and statistics for Manganese additions to cottonseed biodiesel

Identification of outlier in Mn additions to cottonseed biodiesel

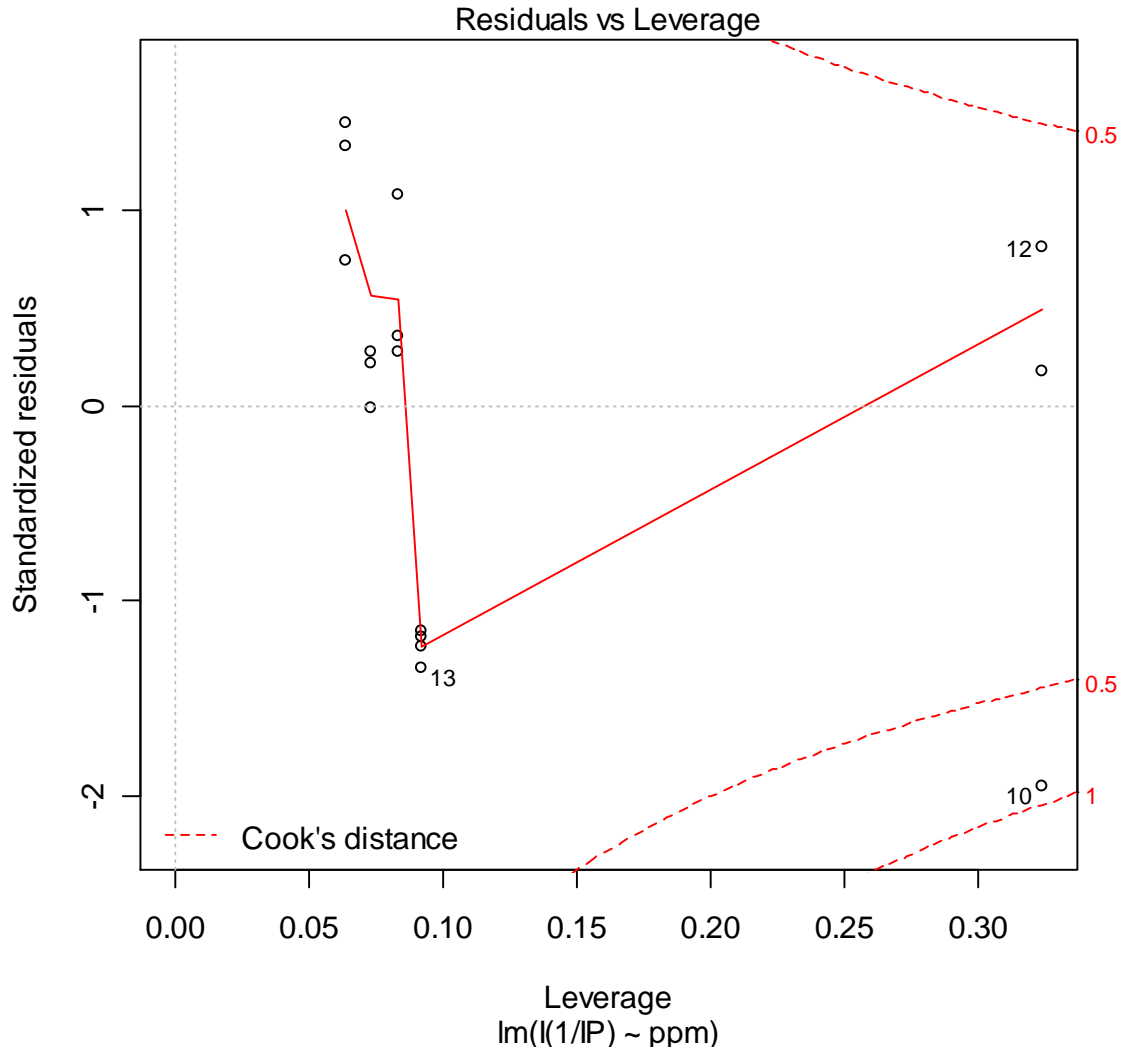


Figure 31
Identification of outlier at data point 10 (Mn add of 5 ppm)

Curve fit and statistics for Manganese in cottonseed biodiesel with outlier removed

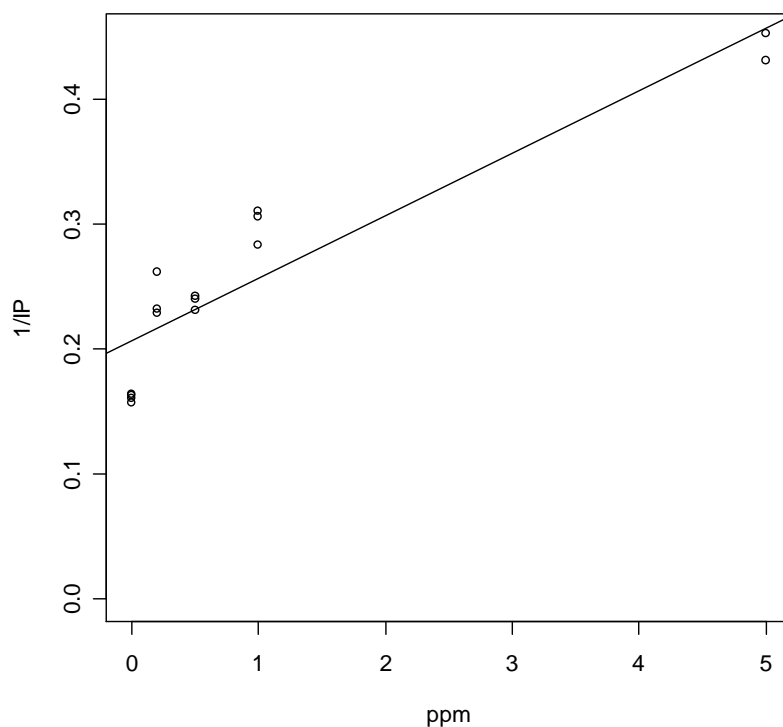


Figure 32

Least squares fit of Manganese additions to cottonseed biodiesel with 1 outlier removed

Min	1Q	Median	3Q	Max
-0.050780	-0.034558	0.007803	0.020252	0.053578
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.207030	0.011231	18.433	1.06e-10 ***
k_1	0.049952	0.005927	8.428	1.26e-06 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 13 DF	p-value
0.03685	13	0.8334	71.04	1.257e-06

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 28

Residuals, Coefficients, and statistics for Manganese additions to cottonseed biodiesel with one outlier removed

Curve fit and statistics for Iron in soybean biodiesel

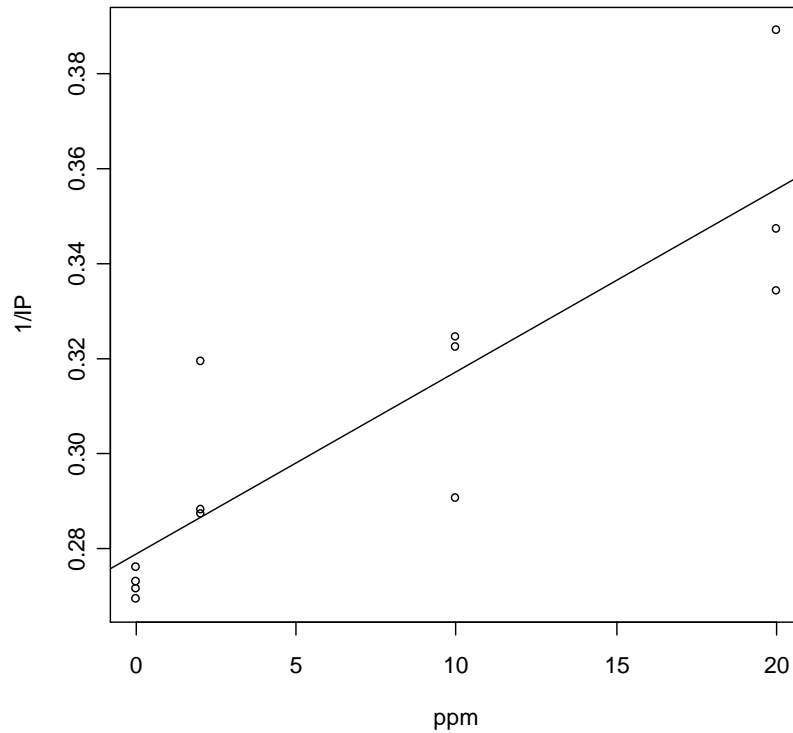


Figure 33
Least squares fit of Iron additions to soybean biodiesel

Min	1Q	Median	3Q	Max
-0.026626	-0.008544	-0.002639	0.005257	0.033339
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.2788816	0.0069736	39.991	2.90e-13***
k_1	0.0038442	0.0006466	5.945	9.66e-05***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.01832	11	0.7411	35.34	9.661e-05

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 29
Residuals, Coefficients, and statistics for Iron additions to soybean biodiesel

Curve fit and statistics for Iron in cottonseed biodiesel

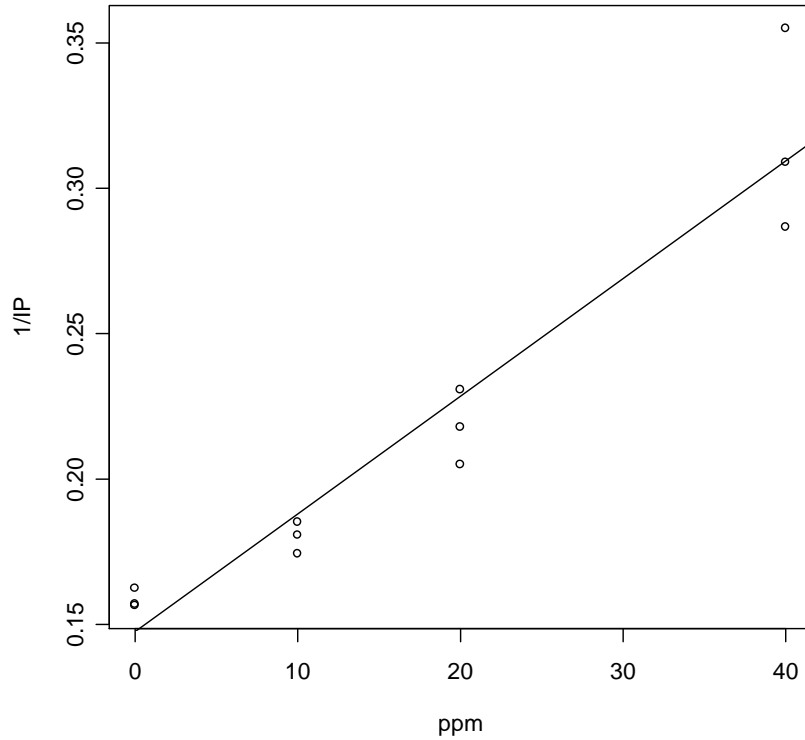


Figure 34

Least squares fit of Iron additions to cottonseed biodiesel

Min	1Q	Median	3Q	Max
-0.023429	-0.011273	-0.001675	0.009239	0.045295
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.1473787	0.0088101	16.73	1.22e-08 ***
k_1	0.0040484	0.0003845	10.53	9.89e-07 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 10 DF	p-value
0.0197	10	0.909	110.9	9.892e-07

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 30

Residuals, Coefficients, and statistics for Iron additions to cottonseed biodiesel

Curve fit and statistics for Cobalt in soybean biodiesel

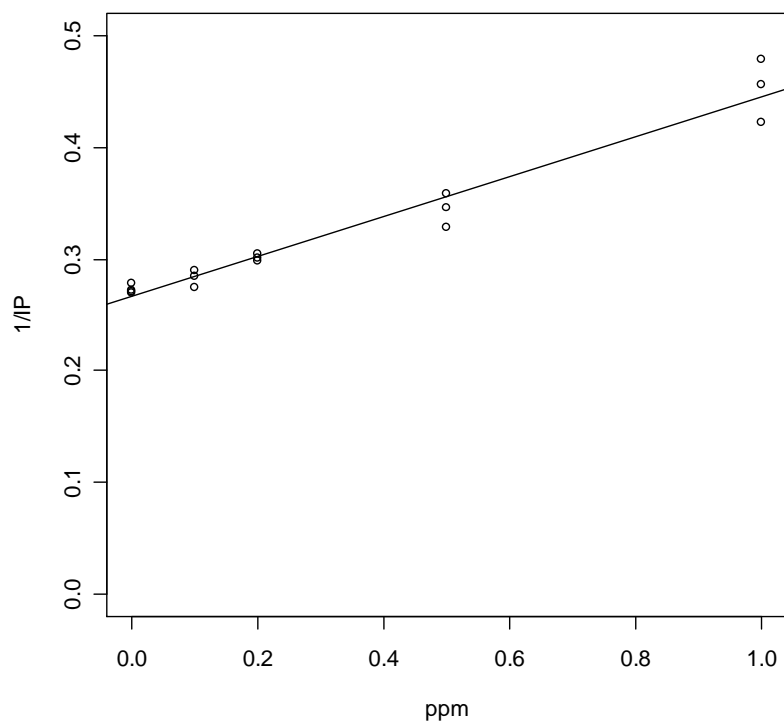


Figure 35
Least squares fit of Cobalt additions to soybean biodiesel

Min	1Q	Median	3Q	Max
-0.028228	-0.005265	0.002518	0.004999	0.032493
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.266217	0.005015	53.09	< 2e-16 ***
k_1	0.179759	0.010157	17.70	5.6e-11 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.01464	14	0.9542	313.2	5.604e-11

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 31
Residuals, Coefficients, and statistics for Cobalt additions to soybean biodiesel

Curve fit and statistics for Cobalt in cottonseed biodiesel

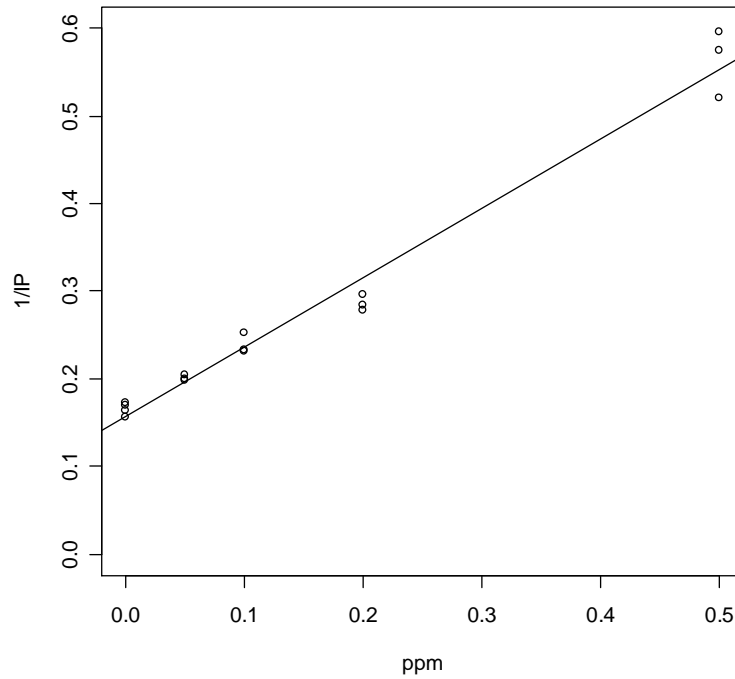


Figure 35
Least squares fit of Cobalt additions to cottonseed biodiesel

Min	1Q	Median	3Q	Max
-0.037554	-0.008814	0.002359	0.013876	0.042534
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.157084	0.007476	21.01	5.50e-12 ***
k_1	0.791241	0.031391	25.21	4.58e-13 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.02222	14	0.9769	635.3	4.579e-13

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 32
Residuals, Coefficients, and statistics for Cobalt additions to cottonseed biodiesel

Curve fit and statistics for Nickel in soybean biodiesel

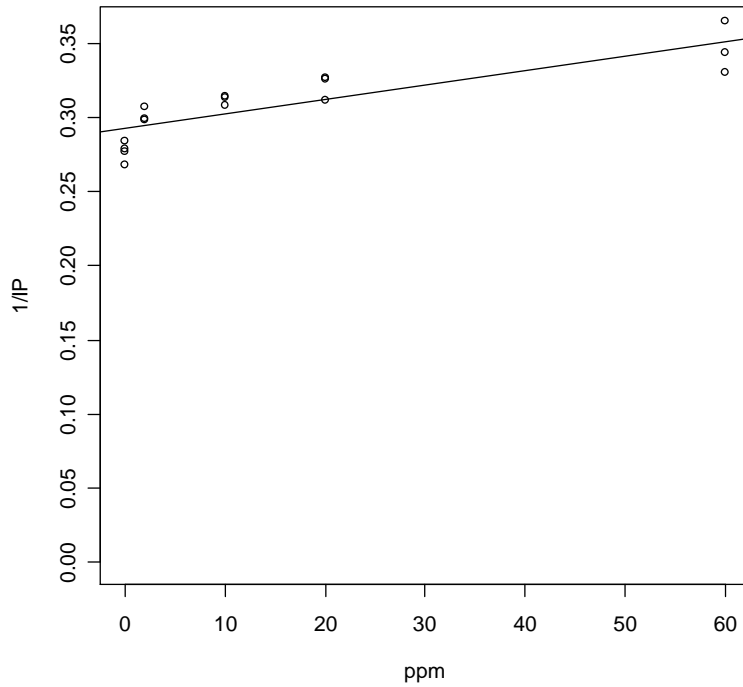


Figure 37
Least squares fit of Nickel additions to soybean biodiesel

Min	1Q	Median	3Q	Max
-0.024500	-0.009890	0.004407	0.012137	0.014694
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.2925961	0.0044285	66.07	< 2e-16 ***
k_1	0.0009754	0.0001596	6.11	2.7e-05 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.01387	14	0.7078	37.33	2.698e-05

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 33
Residuals, Coefficients, and statistics for Nickel additions to soybean biodiesel

Identification of outlier in Ni additions to soybean biodiesel

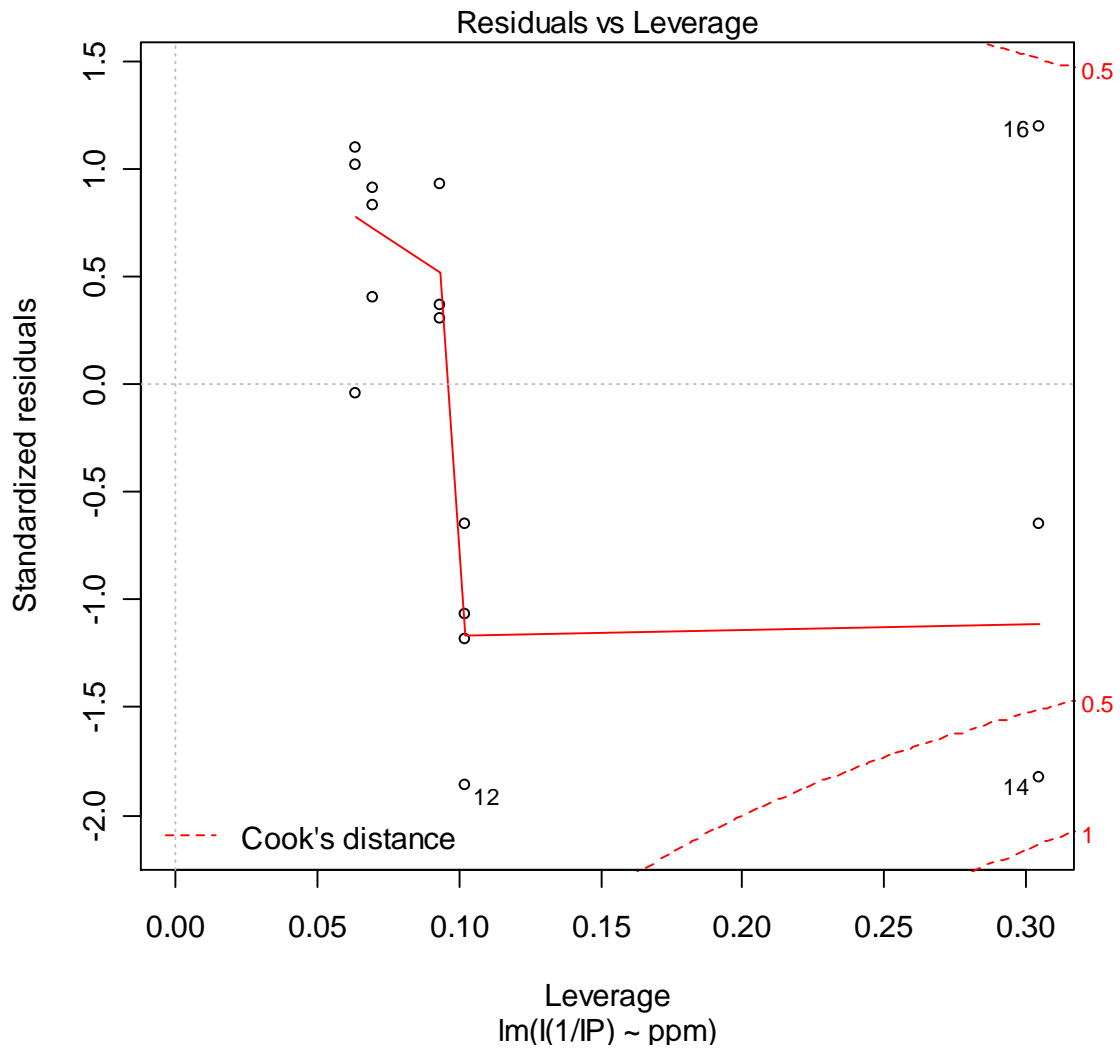


Figure 38
Identification of outlier at 14 (Fe add of 60 ppm)

Curve fit and statistics for Nickel in soybean biodiesel with outlier removed

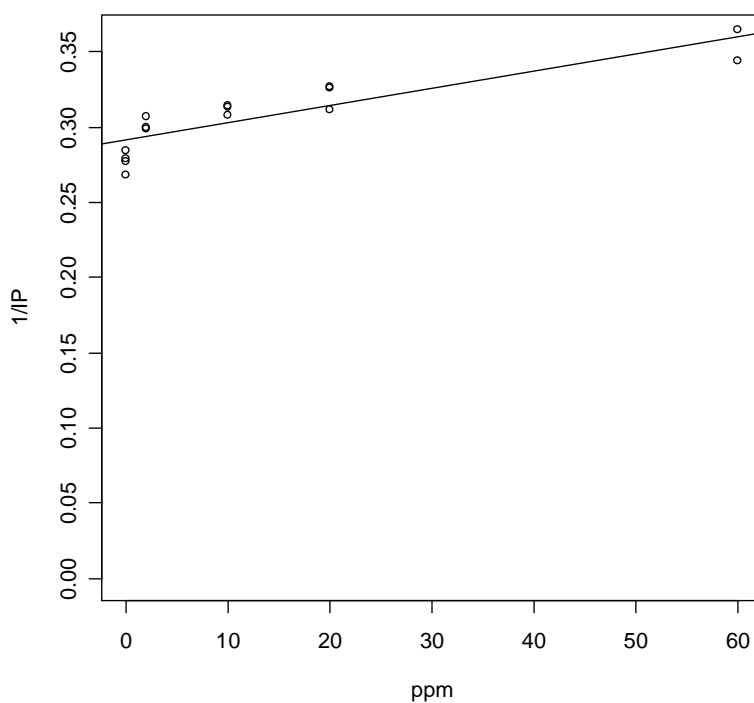


Figure 39

Least squares fit of Nickel additions to soybean biodiesel with one outlier removed

Min	1Q	Median	3Q	Max
-0.023434	-0.010209	0.004683	0.010871	0.012924
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.291530	0.004049	72.009	2e-16 ***
k_1	0.001147	0.000168	6.828	1.21e-05 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 13 DF	p-value
0.01257	13	0.7652	46.62	1.210e-05

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 34

Residuals, Coefficients, and statistics for Nickel additions to soybean biodiesel with one outlier removed

Curve fit and statistics for Nickel in cottonseed biodiesel

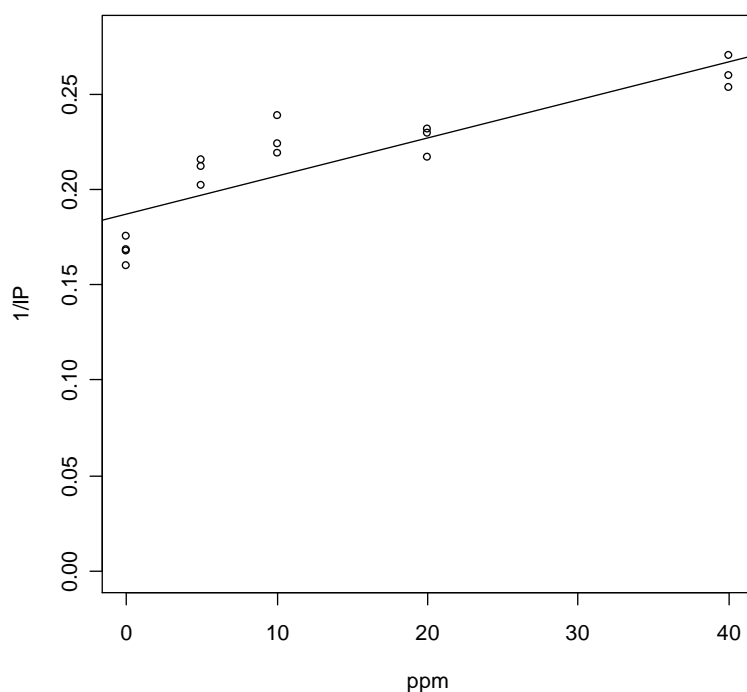


Figure 40
Least squares fit of Nickel additions to cottonseed biodiesel

Min	1Q	Median	3Q	Max
-0.027433	-0.012294	0.002678	0.012527	0.031500
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.1871773	0.0059530	31.442	2.18e-14 ***
k_1	0.0019986	0.0002982	6.702	1.01e-05 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.0169	14	0.7454	44.91	1.008e-05

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 35
Residuals, Coefficients, and statistics for Nickel additions to cottonseed biodiesel

Curve fit and statistics for Copper in soybean biodiesel

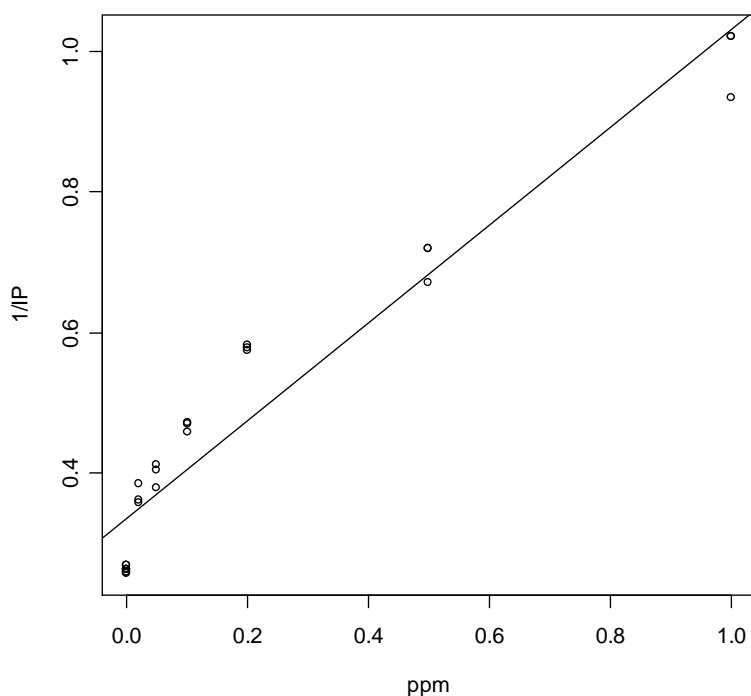


Figure 41
Least squares fit of Copper additions to soybean biodiesel

Min	1Q	Median	3Q	Max
-0.095961	-0.070337	0.008031	0.039961	0.106798
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.33561	0.01541	21.78	< 2e-16***
k_1	0.69493	0.03974	17.49	3.67e-15***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 24 DF	p-value
0.06527	24	0.9242	305.9	3.674e-15

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 36
Residuals, Coefficients, and statistics for Copper additions to soybean biodiesel

Curve fit and statistics for Copper in cottonseed biodiesel

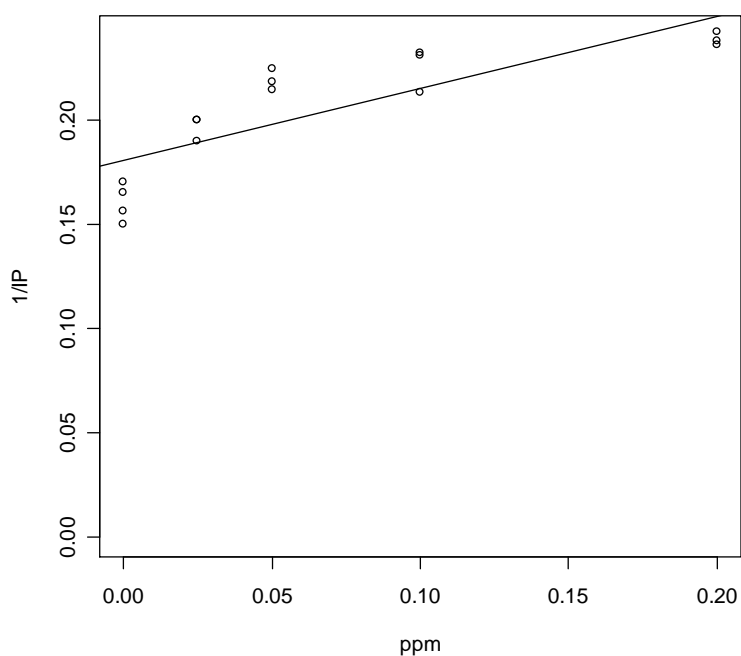


Figure 42

Least squares fit of Copper additions to cottonseed biodiesel

Min	1Q	Median	3Q	Max
-0.0307666	-0.0126754	-0.0007969	0.0159382	0.0267541
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.180692	0.006299	28.685	7.74e-14 ***
k_1	0.345467	0.063116	5.474	8.20e-05 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.01788	14	0.6588	29.96	8.203e-05

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 37

Residuals, Coefficients, and statistics for Copper additions to cottonseed biodiesel

Curve fit and statistics for Zinc in soybean biodiesel

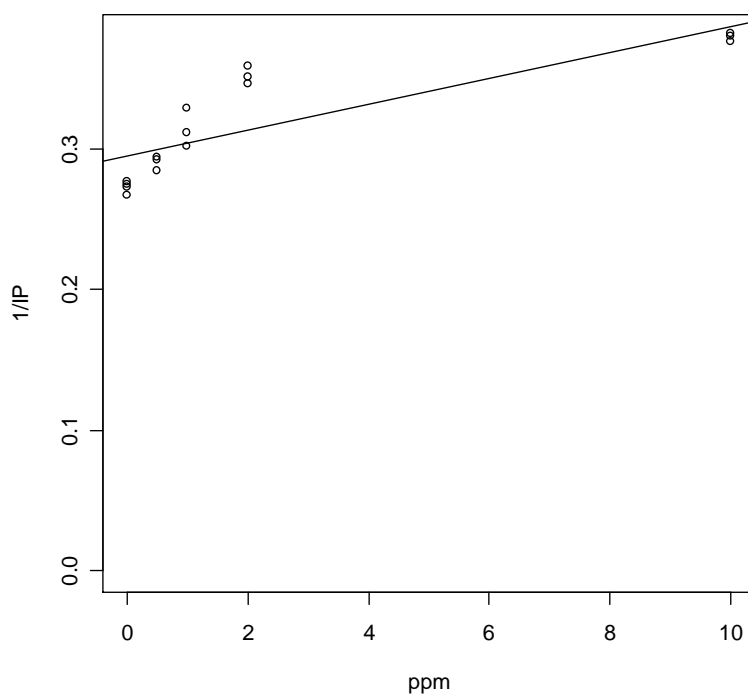


Figure 43

Least squares fit of Zinc additions to soybean biodiesel

Min	1Q	Median	3Q	Max
-0.028519	-0.016515	-0.006456	0.011474	0.044793
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.295185	0.007161	41.222	5.11e-16 ***
k_1	0.009222	0.001612	5.721	5.28e-05 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.02354	14	0.679	32.73	5.284e-05

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 38

Residuals, Coefficients, and statistics for Zinc additions to soybean biodiesel

Identification of outlier in Zinc additions to soybean biodiesel

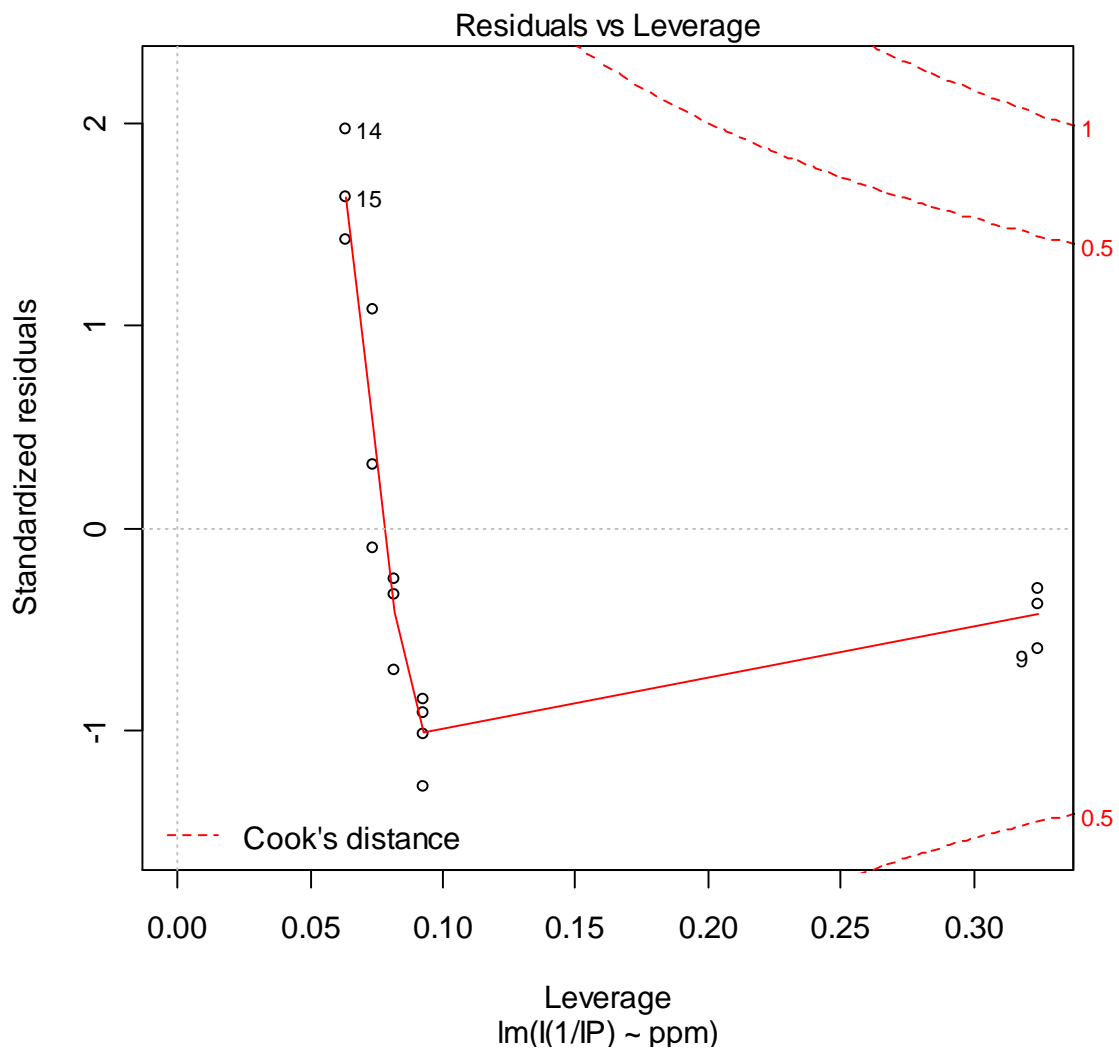


Figure 44
Identification of outlier at 14 (Zn add of 2 ppm)

Curve fit and statistics for Zinc in soybean biodiesel with outlier removed

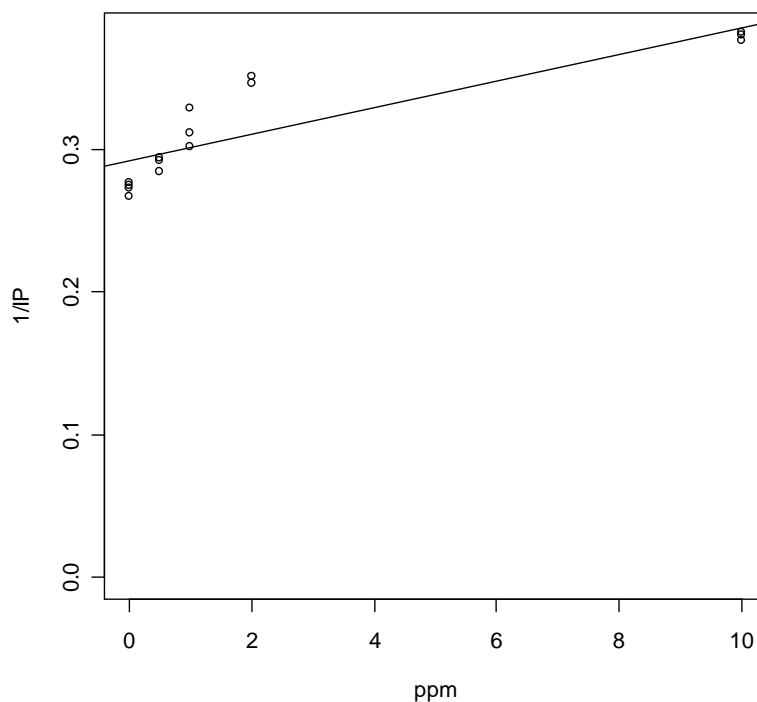


Figure 45

Least squares fit of Zinc additions to soybean biodiesel with one outlier removed

Min	1Q	Median	3Q	Max
-0.025227	-0.014062	-0.004167	0.005586	0.040300
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k ₀	0.291893	0.006492	44.96	1.18e-15 ***
k ₁	0.009342	0.001424	6.56	1.83e-05 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.02078	13	0.7501	43.03	1.826e-05

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 39

Residuals, Coefficients, and statistics for Zinc additions to soybean biodiesel with one outlier removed

Curve fit and statistics for Zinc in cottonseed biodiesel

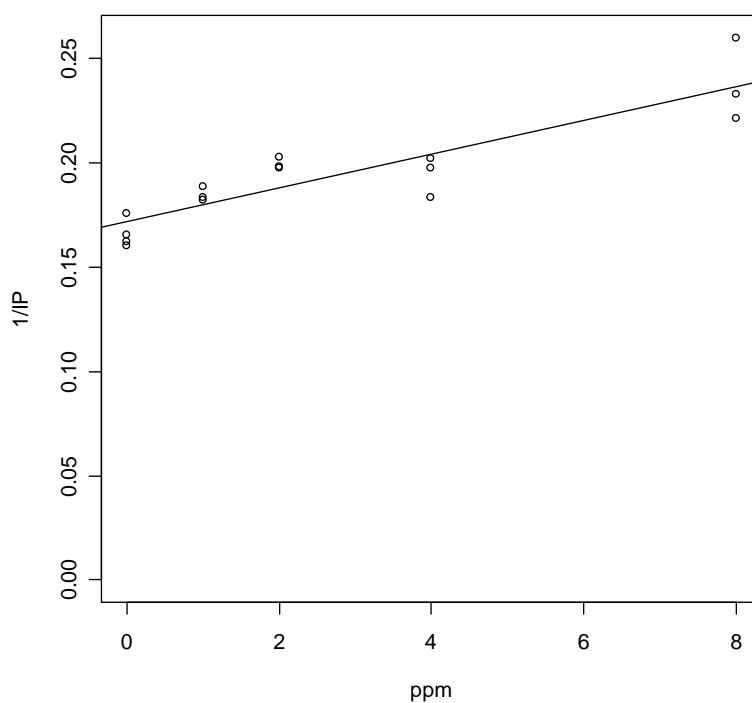


Figure 46

Least squares fit of Zinc additions to cottonseed biodiesel

Min	1Q	Median	3Q	Max
-2.059e-02	-7.417e-03	1.249e-05	8.881e-03	2.323e-02
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.171632	0.004277	40.13	7.42e-16 ***
k_1	0.008110	0.001071	7.57	2.59e-06 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 14 DF	p-value
0.01214	14	0.7897	57.31	2.588e-06

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 40

Residuals, Coefficients, and statistics for Zinc additions to cottonseed biodiesel

Identification of outlier in Zinc additions to soybean biodiesel

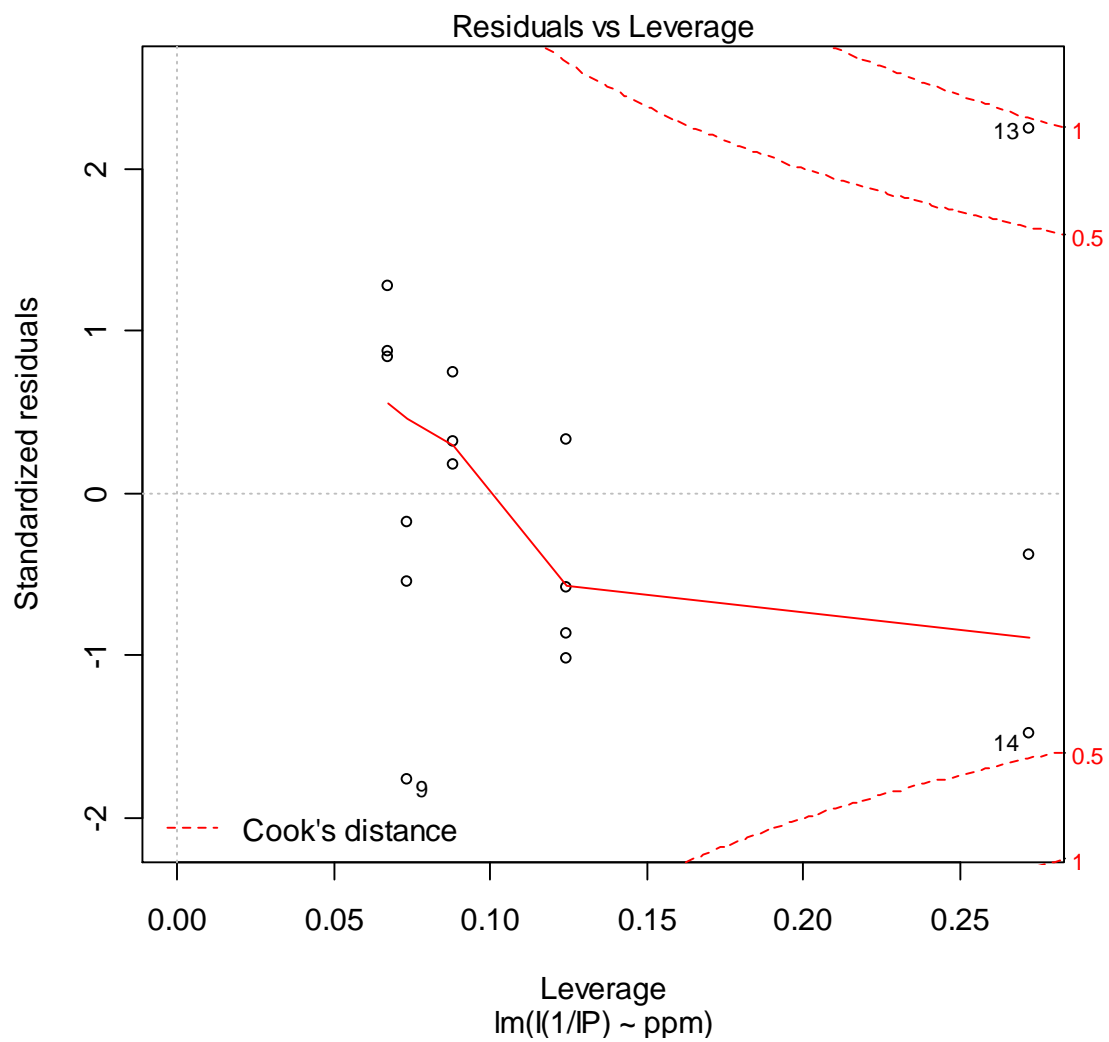


Figure 47
Identification of outlier at 9 (Zn add of 2 ppm)

Curve fit and statistics for Zinc in cottonseed biodiesel

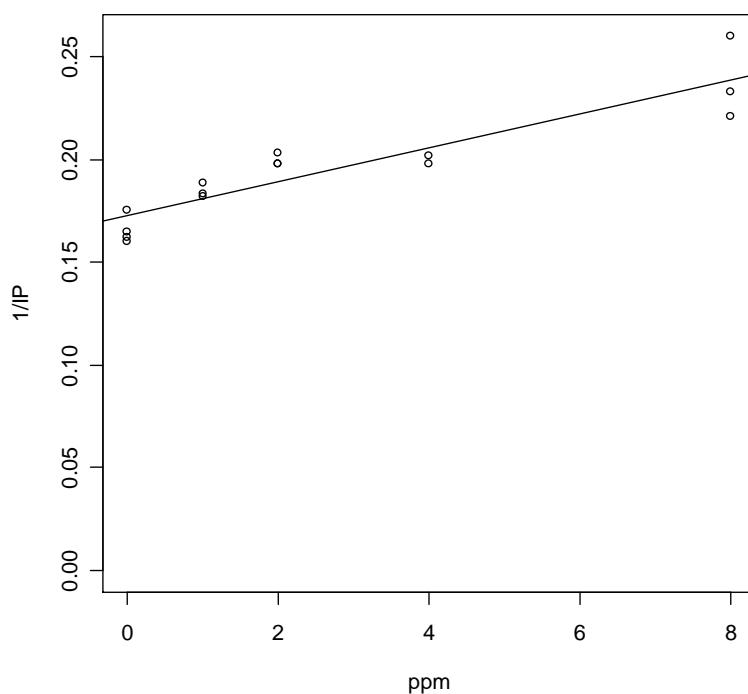


Figure 48

Least squares fit of Zinc additions to cottonseed biodiesel with one outlier removed

Min	1Q	Median	3Q	Max
-0.017726	-0.007751	0.001060	0.008060	0.020776
Coefficient	Estimate	Std. Error	t value	Pr(> t)
k_0	0.1724432	0.0039381	43.788	1.67e-15 ***
k_1	0.0083152	0.0009866	8.428	1.26e-06 ***
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 13 DF	p-value
0.01112	13	0.8334	71.04	1.258e-06

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 41

Residuals, Coefficients, and statistics for Zinc additions to cottonseed biodiesel with outlier removed

The results of the new model are summarized in Table 41 below. In all cases k_0 and k_1 have the correct signs. The statistical significance of the coefficient k_1 , which is the p-value, is the most important statistic shown. It indicates the statistical validity of the coefficient that determines the slope of the curve fit and indicates the likelihood (probability) of obtaining a t-value as high as the one calculated by random chance. The p-value is very good (i.e. very small) for every metal and feedstock combination.

Metal.feed	k_0 (Intercept)	Statistical significance	k_1 (ppm)	statistical significance	Adjusted R-squared
V.soy	0.271726	5.54e-13***	0.147256	1.52e-10***	0.9768
V.cotton	0.191619	4.14e-12***	0.388736	4.05e-12***	0.9685
Cr.soy	0.25549	6.30e-10***	1.44283	8.47e-12***	0.9911
Cr.cotton	0.15040	4.73e-09***	0.55716	1.48e-12***	0.9727
Mn.soy	0.310128	9.99e-12***	0.083787	3.54e-09***	0.9173
Mn.cotton	0.207030	1.06e-10***	0.049952	1.26e-06***	0.8334 (1 outlier)
Fe.soy	0.2788816	2.90e-13***	0.0038442	9.66e-05***	0.7411
Fe.cotton	0.1473787	1.22e-08***	0.0040484	9.89e-07***	0.909
Co.soy	0.266217	< 2e-16 ***	0.179759	5.6e-11 ***	0.9542
Co.cotton	0.157084	5.50e-12***	0.791241	4.58e-13***	0.9769
Ni.soy	0.291530	< 2e-16 ***	0.001147	1.21e-05***	0.7652 (1 outlier)
Ni.cotton	0.1871773	2.18e-14***	0.0019986	1.01e-05***	0.7454
Cu.soy	0.33561	< 2e-16***	0.69493	3.67e-15***	0.9242
Cu.cotton	0.180692	7.74e-14***	0.345467	8.20e-05***	0.6588
Zn.soy	0.291893	1.18e-15***	0.009342	1.83e-05***	0.7501 (1 outlier)
Zn.cotton	0.1724432	1.67e-15***	0.0083152	1.26e-06***	0.8334 (1 outlier)

Table 42
Summary of statistics for equation $1/IP = k_1 * ppm + k_0$

To further test the assumptions of the model a series of statistics were generated from Equation 9:

$$\frac{1}{IP^2} = k_1[M] + k_0$$

Equation 9

This is a variation on Equation 8 which includes the hydroperoxide to hydroperoxide termination reaction but exclude the alkoxy concentration. The results are given below in Table 42. As in the first model with equation 6, the results are not good. Again several of the intercepts have the wrong sign.

Metal.feed	k ₀ (Intercept)	Statistical significance	k ₁ (ppm)	statistical significance	Adjusted R-squared
V.soy	-0.28987	0.0553 .	0.65033	2.34e-08***	0.8919
V.cotton	0.026581	6.02e-06***	0.289916	1.69e-15***	0.9896
Cr.soy	-0.08824	0.158	2.51537	5.52e-12***	0.9671
Cr.cotton	-0.01042	0.637	0.49281	2.06e-08***	0.8938
Mn.soy	0.085626	3.68e-06***	0.084729	7.63e-11***	0.9521
Mn.cotton	0.043689	8.01e-06***	0.026704	2.31e-07***	0.8504
Fe.soy	-0.030669	0.84807	0.019869	0.00348 **	0.4297
Fe.cotton	-0.052137	0.297	0.007503	2.20e-05***	0.7159
Co.soy	0.067210	7.82e-10***	0.130451	1.37e-09***	0.9277
Co.cotton	0.006548	0.52	0.587841	1.15e-09***	0.9295
Ni.soy	8.567e-02	1.75e-14***	6.199e-04	1.62e-05***	0.7279
Ni.cotton	0.0351323	3.96e-10***	0.0008723	2.57e-06***	0.7899
Cu.soy	0.12714	1.72e-07***	0.70793	< 2e-16 ***	0.9672
Cu.cotton	0.033045	1.03e-09***	0.140103	3.17e-05***	0.7011
Zn.soy	0.088168	3.53e-11***	0.006106	6.15e-05***	0.6722
Zn.cotton	0.0290869	1.94e-10***	0.0033342	3.45e-06***	0.781

Table 43
Summary of statistics for equation $1/(IP^2) = k_1 \cdot ppm + k_0$

Testing significance of counter-ions

It is necessary to test for the statistical significance of the chloride and nitrate counter-ions. Data from two metals using the same counter ion are combined. The concentrations of the metals are used to calculate the concentrations of counter-ion. If the change of induction period was caused by the counter-ion then both the metals should have statistical significance. If the metals are statistically significant, then the metal with the greatest concentration range will dominate the model and the metal with the lowest concentration will be rejected (i.e not statistically significant).

Chloride Test

Data generated from the addition of Manganese Chloride and Chromium Chloride in soybean biodiesel are combined. Mn has the greatest concentration range. See the graph 41 and the associated statistics. If Manganese is statistically significant then chloride is not the primary cause of the observed IP reductions.

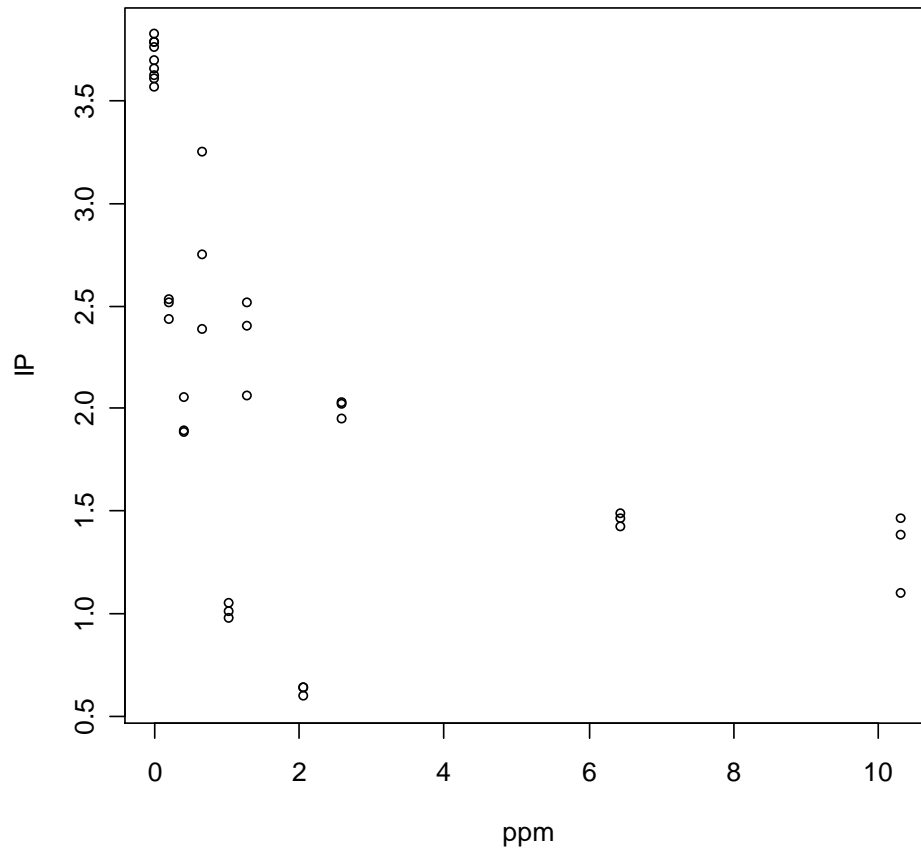


Figure 49
Data for chloride test

Coefficients:

	Estimate	Std. Error	t value	Pr(> t)
(Intecept)	2.22448	0.19999	11.123	1.06e-12 ***
ppm chloride	-0.24381	0.04756	-5.126	1.27e-05 ***
Mn	0.96562	0.29022	3.327	0.00216 **

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05

Table 44
Statistics for Chloride test

Nitrate Test

Data generated from the addition of Iron Nitrate and Copper Nitrate are combined. Iron has the greatest concentration range. The data is for the cottonseed feedstock. See the graph 42 and the associated statistics. If Iron is statistically significant then nitrate is not the primary cause of the observed IP reductions.

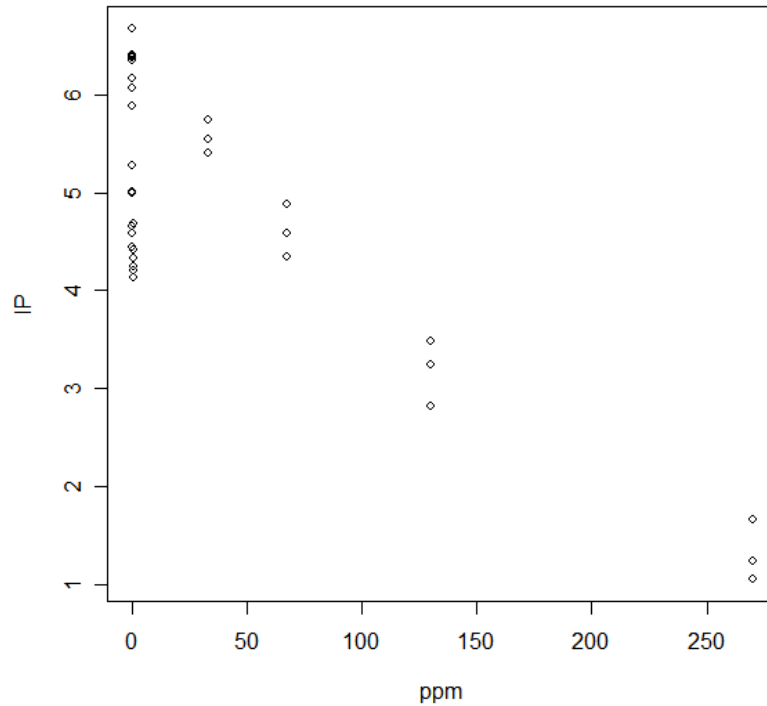


Figure 50
Data for nitrate test

Coefficients:

	Estimate	Std. Error	t value	Pr(> t)
(Intecept)	5.002582	0.161596	30.957	< 2e-16 ***
ppm nitrate	-0.018605	0.001695	-10.980	7.6e-12 ***
Metal Fe	1.071679	0.278188	3.852	0.000596 ***

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05

Table 45
Statistics for nitrate test

In both the chloride and the nitrate tests, the metal (Mn or Fe) with the greatest concentration range is statistically significant and the metals with the lowest concentration (Cr and Cu) are rejected. Thus, the observed changes of induction period are a result of the addition of metal ions.

Effect of Water

Since the metal salts are hydrated it is necessary to determine the effect of water. A test was conducted using the soybean feedstock. See graph 43 and the associated statistics. Additions of water in the range of 20 to 200 ppm have little statistical significance and the p-value does not meet the 95% confidence threshold (i.e. p-value less than 0.05).

Test of significance of water additions

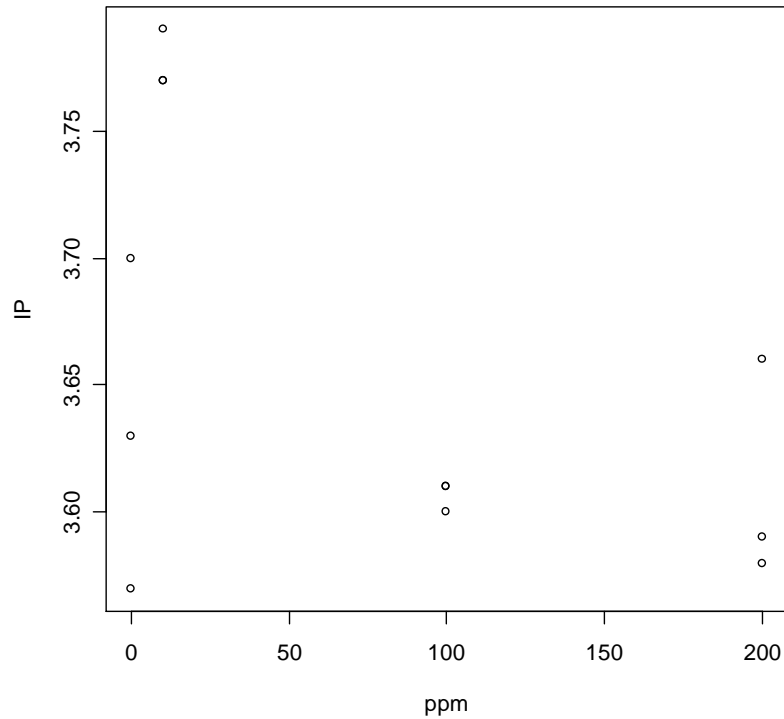


Figure 51
Data for water test

Coefficients :

	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	3.6957015	0.0287497	128.548	<2e-16 ***
ppm water	-0.0005037	0.0002569	-1.961	0.0783
Residual standard error	degrees of freedom	Adjusted R-Squared	F-statistic on 1 and 10 DF	p-value
0.07185	10	0.2777		0.07835

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05

Table 46
Residuals, Coefficients, and statistics for water test

Metal Solubility

The solubility of metal ions during the Rancimat test is another issue to consider. All the salts listed were soluble in anhydrous methanol. But that does not guarantee that they will be soluble in biodiesel. Since solubility is a function of concentration, the metals with the lowest catalytic activity will be most affected. The question is further complicated by the continuous accumulation of oxidation products which may also change metal ion solubility.

In both feedstocks, the Rancimat tests of Fe and Ni produced significant amount of colored insoluble material inside the reaction vessel. At the end of the tests, brown and light green precipitates were observed inside the reaction vessel for Fe and Ni tests, respectively. Under the conditions of the Rancimat test these precipitates could be oxides, hydroxides, organic acid salts or some combination of these. The limited solubility of these ions would remove them from solution and diminish their ability to act as catalysts although it is still possible that these metal precipitates would function as a catalytic surface. The results for Zn are also influenced by solubility. Grey precipitates were observed inside the reaction vessels at the highest Zn ion concentrations.

Blanks over Time

The biodiesel samples used in these experiments are stored in air tight containers in a conventional refrigerator. The question remains is if the biodiesel experienced significant degradation over the time of testing. Data from the blanks of the two feedstocks are collected. See the figure 70 for a graph of the blanks of soybean biodiesel.

These tests were conducted over 55 days. See figure 71 for a graph of the blanks of cottonseed biodiesel. These tests were conducted of 35 days. While it is expected that the induction period of biodiesel will decrease over time, air tight storage in a refrigerator effectively limited oxidation for the duration of the investigation. In both soybean and cottonseed biodiesel the p-values indicates that the statistical correlation to the day number is not significant.

Plot of blanks for soybean biodiesel

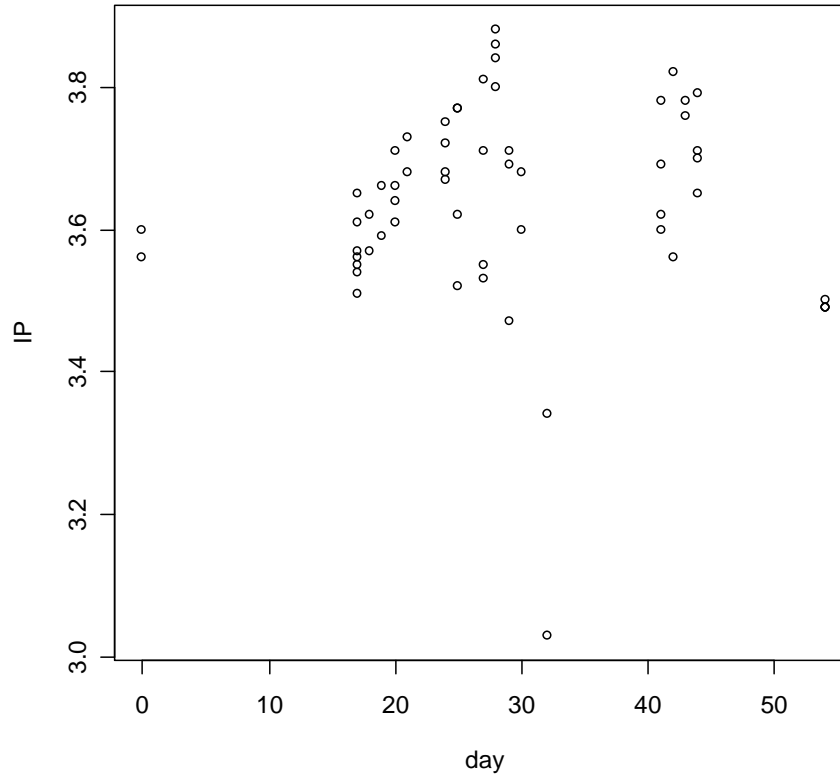


Figure 52

Plot of soybean biodiesel blanks over the duration of the investigation

Min	1Q	Median	3Q	Max
-0.60870	-0.07896	0.01126	0.07871	0.24118
Coefficients	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	3.640	4.727e-02	77.00	<2e-16 ***
Day	-3.026e-05	1.515e-03	-0.02	0.984
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 56 DF	p-value
0.1396	56	-0.01785	0.0003989	0.9841

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05

Table 47

Residuals, coefficients, and statistics of soybean blanks

Plot of blanks for cottonseed biodiesel

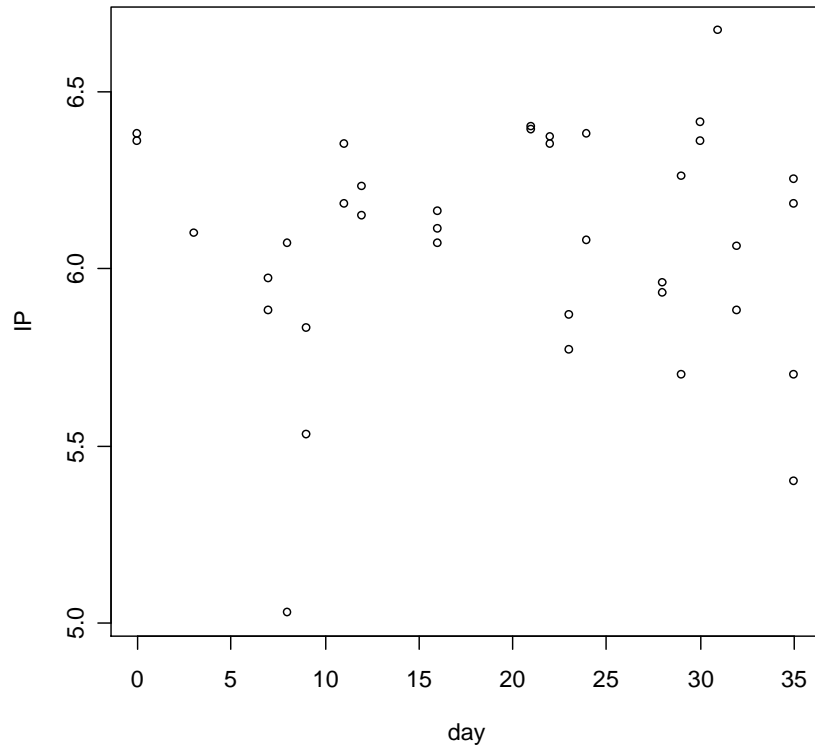


Figure 53

Plot of cottonseed biodiesel blanks over the duration of the investigation

Min	1Q	Median	3Q	Max
-1.03455	-0.18368	0.03981	0.27628	0.58541
Coefficients	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	6.0575770	0.1153364	52.52	<2e-16 ***
Day	0.0008715	0.0051284	0.17	0.866
Residual standard error	degrees of freedom	Adjusted R-squared	F-statistic on 1 and 35 DF	p-value
0.3305	35	-0.02772	0.02888	0.866

Signif. codes: '***' 0.001 '**' 0.01 '*' 0.05

Table 48

Residuals, coefficients, and statistics of cottonseed blanks

Chapter 6 Discussion

General

The data shows that all eight period IV transition metal investigated have the capacity to reduce the induction period of biodiesel. The effect varies by metal and feedstock although there is general agreement between soybean and cottonseed biodiesel for a given metal. There are no examples of a metal which is highly reactive in one feedstock biodiesel while much less reactive in the other.

An equation was derived from the chemistry of oxidation of unsaturated fatty acids and the associated kinetics equations. This equation was used to determine a linear model and statistics were calculated for the fit of this model to the data collected. These statistics were used to evaluate the linear model.[55]

There is a problem with the statistics generated for this first linear model. Based on the assumptions given and the mathematical analysis performed, the signs (positive or negative) of the coefficients are not arbitrary. This is true because the rate constants and the molar concentrations of all species must be non-negative while the coefficient of the constant term should be negative. Yet, table 21 shows that in 5 cases k_0 is positive, in 7 cases k_1 is negative and in 6 cases k_2 is negative. In only 3 of the 16 metal/feedstock combinations did all three coefficients have the correct signs. Removing the term associated with k_2 , which eliminates the hydroperoxide to hydroperoxide termination

reaction from the model results in curve fits which produced coefficients with the correct signs in all 16 combinations.

It is concluded that the high temperatures of DIN EN 14112 and ASTM Specification D6751 suppress at least one of the free radical termination reactions which generate oxidation products. The Rancimat can only measure the reaction products of oxidation, not oxidation itself. It is therefore a qualitative tool used for comparison and not a strictly quantitative analysis of free radical oxidation. The elimination of a termination reaction calls into question the ability of DIN EN 14112 and ASTM Specification D6751 to model “real world” biodiesel oxidation. Using these tests to develop antioxidant systems to stabilize biodiesel against oxidation is also called into question.

While the fatty acid profiles and the antioxidant concentrations of triglycerides will vary over time, the chemistry and kinetics of oxidation will not. It should be noted that the coefficients generated in this study may not be reproduced if the experiments are repeated with biodiesel manufactured from different lots of triglyceride feedstock. Variations in antioxidant concentration and the handling of triglyceride feedstock prior to and during biodiesel manufacture can produce significant variation in the contaminants and antioxidant concentrations which influence the oxidative stability of the biodiesel.[42, 44]

Coefficients

The y-intercept term k_0

This term represents impurities present in the biodiesel samples that promote oxidation and give the samples a finite induction period. These y-intercepts are summarized below in table 49 and graph 54.

metal	k_0 cotton	k_0 soy
V	0.191619	0.271726
Cr	0.1504	0.25549
Mn	0.20703	0.310128
Fe	0.147379	0.278882
Co	0.157084	0.266217
Ni	0.187177	0.29153
Cu	0.180692	0.33561
Zn	0.172443	0.291893
mean	0.174228	0.287684
std dev	0.021293	0.025809

Table 49
Summary of the values of the y-intercept terms k_0

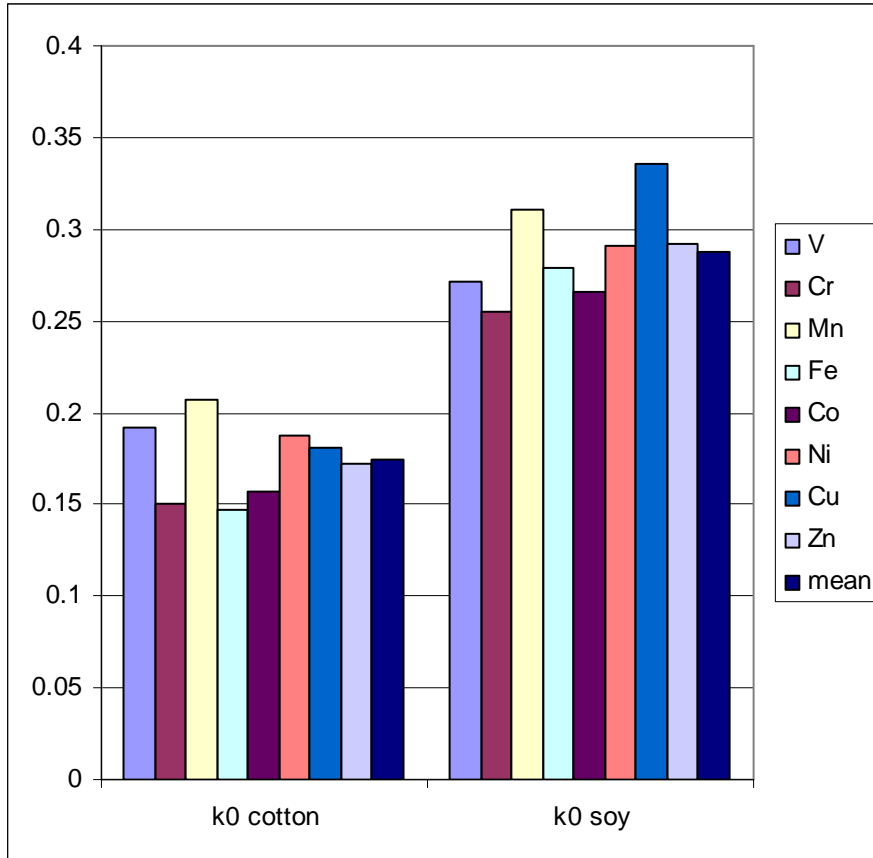


Figure 54
Summary of the coefficients k_0 demonstrating agreement

From Equation 8 it follows that when the metal concentration is zero, the inverse of the intercept should approximate the IP of the blanks. Table 50 contains the inverses of the means values from Table 49 and the inverses of the mean minus one standard deviation and plus one standard deviation. Table 50 also contains the mean values of the blanks given in Table 47 and 48. The values of the blanks fall easily within the range determined by the inverse of the means plus or minus one standard deviation.

	cotton	soy
$(\text{mean } k_0 - 1 \text{ s.d.})^{-1}$	6.538711	3.818603
$(\text{mean } k_0)^{-1}$	5.74	3.48
$(\text{mean } k_0 + 1 \text{ s.d.})^{-1}$	5.114548	3.189864
mean of blanks	6.06	3.64

Table 50

Ranges of inverses of means of k_0 plus or minus one standard deviation and comparison to the mean value of the blanks

Good agreement of these coefficients k_0 helps to demonstrate the validity of the mathematical model used. Precise agreement is unrealistic due to the indirect nature of the Rancimat test which measure oxidation products, not oxidation itself.

The slope term k_1

The situation for the slope terms is more complex. Tables 51 and 52 summarized the ranked slope terms for soybean and cottonseed biodiesel.

soybean	k_1
Ni	0.001147
Fe	0.0038442
Zn	0.009342
Mn	0.083787
V	0.147256
Co	0.179759
Cu	0.69493
Cr	1.44283

Table 51

Ranked terms k_1 for soybean biodiesel

cottonseed	k_1
Ni	0.0019986
Fe	0.0040484
Zn	0.0083152
Mn	0.049952
Cu	0.345467
V	0.388736
Cr	0.55716
Co	0.791241

Table 52
Ranked terms k_1 for cottonseed biodiesel

Recall that the k_1 term is a measure of the catalytic activity of the metal investigated. A higher slope indicates an increased rate of oxidation and a greater reduction of the induction period of biodiesel. The k_1 term can be used to rank the catalytic activity of these metals. The weakest metals are Nickel, Iron, Zinc, and Manganese in that order for both feedstocks. Vanadium, Chromium, Cobalt, and Copper are the most active although the order changes with feedstock. There are three low catalytic activity metals (Fe, Ni, and Zn) with $k_1 \leq 0.01$. There is one moderate activity metal (Mn) with $0.01 < k_1 \leq 0.1$. There are four high activity metals (V, Cr, Co, and Cu) with $0.1 < k_1$. Of the four high activity metals, Vanadium and Cobalt were more active in cottonseed biodiesel. Chromium and Copper were more active in soybean biodiesel. Fe, Ni, and Zn also had the lowest solubility (i.e. the great precipitate formation) of the metals tested. These results are summarized in Table 53.

feedstock	$k_1 \leq 0.01$	$0.01 < k_1 \leq 0.1$	$0.1 < k_1$
soybean	Fe, Ni, and Zn	Mn	V, Co, Cu, Cr
cottonseed	Fe, Ni, and Zn	Mn	Cu, V, Cr, Co

Table 53
Summary of ranked catalytic activity

Photochemistry

The Carbon to Hydrogen bond of bis-allylic Hydrogen has a reported bond energy of 52 kcal/mole. [14] It has been reported that biodiesel degrades when exposed to visible light. [14] Using the methods of photochemistry, it is possible to calculate the wavelength of light that corresponds to a specific chemical bond. Since the bis-allylic Hydrogen is reported to be the primary source of biodiesel oxidation, the wavelength of light corresponding to its 52 kcal/mole bond energy was calculated.

$$\text{Energy (ergs)} = h \cdot \nu$$

Here h is Planck's constant ($6.612 \cdot 10^{-27}$ erg sec) and ν is the frequency of light.

$$E \text{ (ergs / mole)} = N \cdot h \cdot \nu$$

Here N is Avogadro's number ($6.02 \cdot 10^{23}$ inverse moles).

$$\nu = c / \lambda$$

Here c is the speed of light ($3 \cdot 10^8$ meters per second) and wavelength is measured in meters.

$$E = N \cdot h \cdot c / \lambda$$

$$E = (N \cdot h \cdot c / \lambda) / (4.184 \cdot 10^{10})$$

The value $4.184 \cdot 10^{10}$ converts from ergs to kilocalories.

$$E = (2.856 / \lambda) * 10^{-5}$$

$$\lambda = (2.856 / E) * 10^{-5} * (10^9)$$

Convert wavelength from meters to nanometers.

$$\lambda = (2.856 / E) * 10^4$$

This formula can be used to calculate the wavelength of light corresponding to a given bond energy E.

$$\lambda = (2.856 / 52) * 10^4$$

Input the bis-allylic Hydrogen bond energy of 52 kcal / mole.

$$\lambda = 549 \text{ nm}$$

This wavelength falls within the visible light spectrum with a yellow-green color and helps explain the reported light sensitivity of biodiesel.

Applications of photochemical free radical reactions

Induction period test

The revised linear model (Equation 8) was developed from the assumption that the heat of the Rancimat test caused the peroxy to peroxy free radical termination reaction to either dissociate or decompose before rearrangement reactions could produce oxidation products. For this reason the k_2 term was removed from the model.

The calculation above indicates that visible light could be used to produce bis-allylic hydroperoxides and the corresponding free radicals. In the presence of light with the correct wavelength (yellow-green) and air (oxygen) hydroperoxides will form.



At room temperatures the peroxy to peroxy termination reaction would proceed to rearrangement reactions producing oxidation products. These could be collected and the induction period determined as in the Rancimat determination but with the oxidation reactions being accelerated by visible light instead of heat. The visible light needed could be produced by the correct choice of light emitting diodes, or incandescent lamps. This method would be a different method of determining an induction period for biodiesel than the standard test as described by DIN EN 14112 and ASTM Specification D6751. If it includes the peroxy to peroxy termination reaction such a test could better represent “real world” biodiesel oxidation. This test method would also be applicable to other fatty acid, fatty acid esters and triglycerides which contain bis-allylic hydrogen.

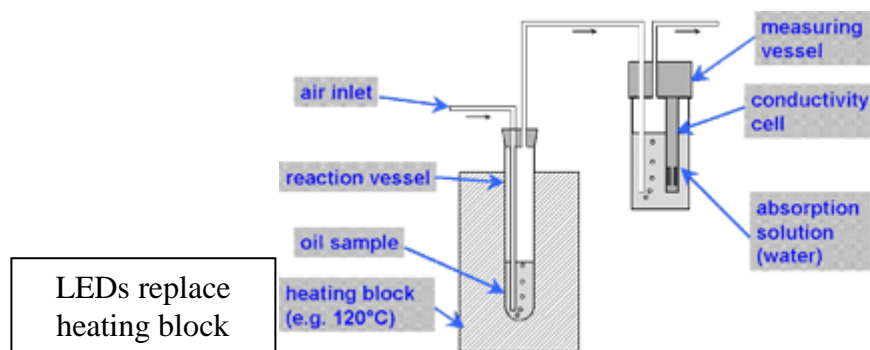
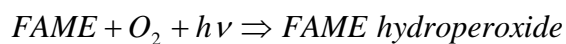


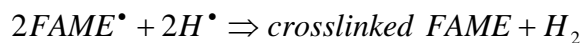
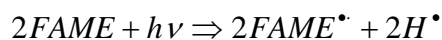
Figure 55
Schematic of modified Rancimat type induction period tester

Cetane booster/fuel

Photochemical free radical formation could be used to synthesize hydroperoxides as Cetane boosters of liquid transport fuels for compression ignition engines (diesel). FAME hydroperoxides mixtures could also be used as transportation fuels themselves. These hydroperoxides could be stabilized with the same antioxidants that have been studied to stabilize biodiesel itself. Sources of metal contamination would need to be minimized.

*Lubricants*

Photochemical free radical formation could also produce cross linking leading to the production of high molecular weights products. These could be useful as lubricants and lubricity additives for transportation fuels. In the presence of a hydrogenation catalyst and Hydrogen, free radicals created by the excitation from visible light could reduce the number of sites of unsaturation resulting in partially hydrogenated FAME dimers.



OR



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ABSTRACT**CATALYTIC EFFECTS OF PERIOD IV TRANSITION METALS IN THE
OXIDATION OF BIODIESEL**

by

BRADLEY R CLARK

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Advisor: Dr. K. Y. Simon Ng**Major:** Alternative Energy Technology**Degree:** Masters of Science

Transition metals have the ability to catalyze free radical autoxidation of unsaturated fatty acid methyl esters (i.e., biodiesel). The catalytic effects of the eight period IV transition metals: V, Cr, Mn, Fe, Co Ni, Cu and Zn in soybean oil and cottonseed oil-based biodiesel are investigated. All metals produced a reduction of the induction period of biodiesel, although there are considerable differences in their catalytic capacity. The amount of reduction is a function of metal selected, the concentration of the metal and the feedstock of the biodiesel. A linear model describing the algebraic relationship between metal concentration and induction period was devised. A least squares fit was used to fit a curve to the induction period data. Good results were only achieved after eliminating one of the free radical termination reactions in the equation of the linear model. This implies that the high temperature of Rancimat run under DIN EN 14112 suppresses one free radical termination reaction and calls into question whether or not this test represent “real world” biodiesel oxidation. The reported bond energy of bis-allylic hydrogen was used to calculate the wavelength of visible light which would lead

to free radical formation. The controlled production of hydroperoxides could lead to photochemical methods to test oxidation stability and to produce value added products from fatty acid methyl esters such as cetane boosters, lubricants and fuels.

AUTOBIOGRAPHICAL STATEMENT

Bradley R. Clark has earned a B.S. in Chemistry from Saginaw Valley State University and a M.A. in Mathematics for Wayne State University. He has worked in specialty chemicals, academia and consulting. He is currently employed by the Michigan Economic Development Corporation as a Technology Development Manager.