Investigation of the Effects of Structural Characteristics on the Sooting Tendencies of Lactones

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August 2023

Abstract

As climate change is undeniably one of today's greatest issues, one area of interest is finding fuels with lower emissions, which can be quantified using sooting indices. In this paper, we use the yield sooting index (YSI), which has values positively correlated with soot yield, to characterize fuel compounds. We measured the sooting tendencies of γ-valerolactone and 7 other structurally similar lactone compounds using the same sooting index for the first time, allowing for discovery of potential relationships between chemical structure and sooting tendency. Specifically, we found that sooting tendency increases with both side chain presence and length, with its presence increasing the YSI by much more, while ring size has either no effect or an undetermined one, and ring double bonding seems to decrease YSI.

Keywords: biofuel, lactone, sooting tendency, yield sooting index (YSI), group contribution model (GCM)

Acknowledgements

This research was conducted in the Pfefferle Lab at the Department of Chemical and Environmental Engineering of Yale University under the direct guidance of Dr. Charles McEnally. The author would like to thank graduate student Zhanhong 'Aurora' Xiang for her mentorship and supervision. The author would also like to thank Dr. Christopher Hogue of Choate Rosemary Hall for teaching experimental techniques and guiding literature study in preparation for the summer research.

Commitments on Academic Honesty and Integrity
We hereby declare that we

1. are fully committed to the principle of honesty, integrity and fair play throughout the competition.

2. actually perform the research work ourselves and thus truly understand the content of the work.

3. observe the common standard of academic integrity adopted by most journals and degree theses.

4. have declared all the assistance and contribution we have received from any personnel, agency, institution, etc. for the research work.

5. undertake to avoid getting in touch with assessment panel members in a way that may lead to direct or indirect conflict of interest

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7. observe the safety regulations of the laboratory(ies) where we conduct the experiment(s), if applicable.

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We understand and agree that failure to honour the above commitments may lead to disqualification from the competition and/or removal of reward, if applicable; that any unethical deeds, if found, will be disclosed to the school principal of team member(s) and relevant parties if deemed necessary; and that the decision of YHSA is final and no appeal will be accepted.

(Signatures of full team below)

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Name of team member: David Wang

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1 Introduction

Climate change is one of the key concerns of global society today. As atmospheric pollution continues to accumulate and the Earth's climate continues to warm, the priority has shifted from reversing these effects to stopping their growth by reaching carbon neutrality as soon as possible. To do so, the transportation industry has become the focus of much interest as a sector that produces a significant yet reducible amount of pollution. One way to reduce those emissions is by choosing high-performance, renewable fuels that burn more cleanly.

Specifically, a sizable portion of fuel emissions comes in the form of soot — the carbonaceous, particulate products of incomplete combustion. Soot is often categorized under the PM 2.5 group of particulate emissions (having average diameters under 2.5 microns), which cause up to 9 million global deaths per year [1]. As well as its health risks, soot has many severe environmental impacts. Soot particles in the atmosphere absorb incident sunlight due to their black color, contributing to global warming [2]. Additionally, in airplane emissions, soot provides nucleation sites for ice crystals in contrails, which reflect outgoing light back into the Earth's atmosphere, thereby trapping heat and causing further radiative forcing [3]. In fact, contrails are the largest source of aviation-related global warming. However, soot only has an average atmospheric lifetime of around two weeks, meaning that any reduction in soot emissions would quickly take effect. In contrast, with a centuries-long lifetime, any reduction in CO_2 emissions would not be observable for a long time.

Because of the severe effects of soot emissions, it is an important objective of fuel research to find lower-sooting compounds to use as alternative fuels or fuel additives. This is especially true in industries such as aviation: in such areas, completely shifting to electrical energy is currently impossible, so finding alternative fuels wtih lower sooting is the only way to reduce environmental impacts. As a result, sooting indices have been developed that quantify the soot yield for a single compound in a particular flame setup. By gathering a database of existing sooting tendencies, not only is it possible to find the most sustainable fuels to use as additives to combat climate change, but it is also possible to make predictive models and

find structure property relationships that will allow us to systematically search for optimal fuels. The current industry standard is the smoke point (SP) index [4]. In this paper, we use the yield sooting index (YSI), invented by McEnally and Pfefferle [5] to characterize a series of lactones. The advantages of YSI over SP are that it requires much smaller volumes of fuel (<100 μl for YSI, 10-20 ml for SP), data is taken objectively, and it has a wider dynamic range.

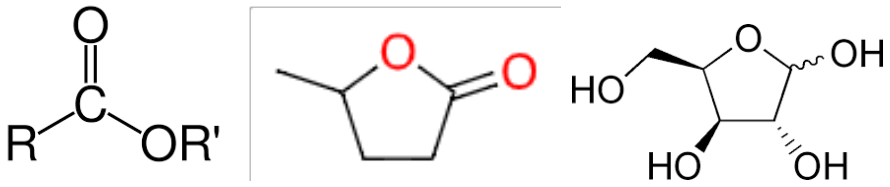
The objective of this study was to investigate the sooting tendencies of a set of 8 lactones. Lactones are cyclic esters that are of interest in fuel research because of previous literature promoting the viability of γ-valerolactone as a fuel additive. In fact, ours was the first study to investigate the sooting tendencies of such a series of lactones using a single sooting index, which will allow for better understanding of structure-property relationships (i.e. the relationship between chemical structure and sooting tendency) for lactones. These 8 compounds were selected to allow several degrees of freedom around γ-valerolactone through which structure-property relationships could be explored, including the presence and length of side chains, ring size, and the presence of double bonding in the ring.

Section 2 will include information on purity and vendors for the compounds studied in this paper, as well as brief summaries on the sooting index and simulations used in this study. Section 3 will present and analyze the data gathered on the lactones' sooting tendencies, as well as the structure-property relationships they reveal. Additionally, some future directions for research will be proposed. Section 4 is a summary of this study's conclusions.

2 Matierals and Procedure

2.1 Acquired Compounds

Lactones are cyclic esters, whereby the groups usually denoted by R and R' (Fig. 1a) are joined. The nomenclature for lactones is usually of the form X-Ylactone, in which X is a Greek letter denoting the ring size and Y is a prefix denoting the total carbon number. For



(a) (b) (c)

Figure 1: (a) A generalized ester structure, where R and R' denote any other functional groups. (b) γ-valerolactone. γ indicates that it has a five-membered ring, and valero indicates that it has a total of five carbons. (c) xylose in its furanose configuration, which is structurally similar to GVL

example, for γ-valerolactone (GVL), as shown in Fig. 1b, γ- indicates a 5-membered ring (of which 4 are carbons) and valero- indicates a total of 5 carbons. One reason lactones are compounds of interest in renewable fuel research is that one of them, GVL has already been identified as a valid candidate for fuel additives: in a 2014 paper, Bereczky et al. performed engine studies on GVL as an additive to fossil and biodiesel, noting a slight engine performance decrease with the addition of GVL but a significant (up to 47%) decrease in soot formation in the exhaust [6].

Furthermore, lactones are easy to synthesize: due to their structural similarity to esters, which are found in vegetable oils, they can be industrially produced from esters. Some lactones have similar structures to sugars, allowing for another production method. For example, γ-valerolactone can be made from xylose's furanose configuration (shown in Fig. 1c).

The acquired compounds are listed in Table 1. Toluene, n-heptane, and isooctane were obtained from Sigma-Aldrich at 99.8%, 99%, and >99% purity, repsectively. α-Angelica lactone was obtained at 98% purity from Thermo Scientific. 98% γ-valerolactone, 98% δ-valerolactone, 99% δ-caprolactone (also known as δ-hexanolactone), and 99% ϵ-caprolactone were obtained from TCI. 98% γ-butyrolactone was obtained from Sigma Aldrich and 98% γ-caprolactone was obtained from Acros. γ-heptanolactone was obtained from TCI at >98.0% purity. 4-pentenoic acid and 5-hexenoic acid were obtained from Thermo Scientific, both at 98% purity.

The 8 lactones were selected to allow us to study the effects of side chain presence/length, ring size, and ring double bonding on lactone sooting. The effect of side chain presence could be studied from comparing GBL, which has no side chain, with GVL, which has a methyl group, or DVL with DCL, for the same comparison. The effect of increasing side chain length could be studied from GVL, GCL, and GHL, which have side chain lengths of 1, 2, and 3 carbons, respectively. Ring size effects could be studied from GBL (5-membered, no side chain), DVL (6-membered, no side chain), and ECL (7 membered, no side chain), or GVL and DCL, for a comparison between 5 and 6 membered rings with a methyl side chain. Finally, the effect of double bonding in the ring could be studied from GVL and AAL, in which the latter has one C=C double bond in the ring and the former doesn't. Therefore, despite the small set of 8 lactones, we were able to obtain preliminary measurements that can hint at possible structure-property relationships between the aforementioned factors and sooting tendency.

Additionally, a study by De Bruycker et al. [7] suggests a potential four- or six-centered reaction, whereby lactones can decyclize into alkenoic acids. Therefore, testing alkenoic acids that correspond to tested lactones could also suggest reaction pathways, by comparing the YSIs of the acids and lactones. If, for example, GVL and 4-pentenoic acid — its associated alkenoic acid — had identical YSIs, that could suggest that the ring opening reaction is dominant for GVL, and possibly for other related lactones. Therefore, we also studied 4-pentenoic acid (4PA) and 5-hexenoic acid (5HA) to determine if the pathways suggested by De Bruycker et al. are relevant.

2.2 Yield Sooting Index (YSI)

The Yield Sooting Index (YSI) is a relative sooting index that quantifies the soot produced by a compound based on the maximum soot volume fraction in a methane/nitrogen coflow nonpremixed flame doped at a 1000ppm concentration with that compound. YSI is defined such that a lower YSI indicates lower soot yield from the corresponding compound. Tests were done on a Yale coflow burner [8]. Soot volume fraction data was gathered via line-of-

sight spectral radiance (LSSR), which integrates the light intensity at 660 nm over 100 ms at 5Hz. The burner was allowed to run while doped with the test compound for 5 minutes to let the dopant achieve an adsorption/desorption equilibrium with the fuel line walls, after which LSSR data was taken for 5 minutes. A schematic for the burner setup is in Fig. 2.

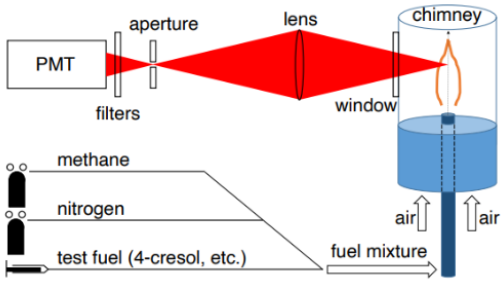


Figure 2: Yale coflow burner with LSSR setup [9]

The calculation for YSI is as follows:

$$\mathrm{YSI_{TC}} = (\mathrm{YSI_A} - \mathrm{YSI_B}) \times \frac{\mathrm{LSSR_{TC}} - \mathrm{LSSR_B}}{\mathrm{LSSR_A} - \mathrm{LSSR_B}} + \mathrm{YSI_B} \tag{1}$$

Subscripts indicate the compound with which the value is associated. Compounds A and B have set YSIs that are used as endpoints for the YSI scale, while TC is the test compound. Equation 1 fits the test compound's LSSR value onto the line that is defined by the YSIs and LSSRs of A and B to determine the YSI of the test compound. For this experiment, compounds A and B were heptane and toluene, with YSIs of 36.0 and 170.9, respectively. These values were determined so that benzene would have a YSI of 100 and extrapolating a graph of YSI vs. carbon number for alkanes would give a hypothetical 0 carbon alkane a YSI of 0. Isooctane is also always included in experiments as an internal standard to ensure the experiment is running properly. Final YSI values are calculated from the average of three independent measurements.

In this experiment, we also calculated the YSIs of each compound using a group contribution model (GCM) YSI estimator [10] and compared the prediction with the measurement. Differences between these two values could suggest the involvement of more complex reactions not accounted for by the predictive model, while also revealing directions for future

improvement. The predictive model is trained on over 600 previously measured YSIs, by decomposing each hydrocarbon into its carbon-centered fragments, and computing the YSI contribution of each fragment via multiple linear regression. By doing the same to any given untested compound, it can repeat the same decomposition process and calculate the compound's YSI as a linear combination of the carbon centered fragments and their respective YSI contributions.

However, one shortcoming of this model is inherent to the way it decomposes molecules: because it only considers immediate neighbors to each carbon atom, it cannot predict the effects of non-nearest neighbor interactions, or NNNIs. Though NNNIs do not usually occur, situations in which they do often involve interested chemistry deserving future study; therefore, comparing measured and predicted YSIs allows us to identify such cases. Another current limitation of the predictive model is the lack of training data: although there are already over 600 compounds in its training set, there are still many functional groups not sufficiently represented. One of them, which is essentially identical to the carboxylic acid functional group but in a ring, is present in the lactones: it is the carbon double bonded to an oxygen and single bonded to another oxygen and another carbon. There is only one occurence of this group in the training data, leading to an extremely high error margin in the estimator. The predicted values for each lactone are also listed in Table 1.

2.3 Simulations

Molecular dynamics and ReaxFF simulations were run by collaborators at Colorado State University and Penn State University to determine potential reaction pathways, in groups led by Prof. Seonah Kim and Prof. Yuan Xuan. ReaxFF simulations involve calculating bond orders from atomic distances at every iteration, allowing it to simulate bond breakage and formation. In the simulation itself, a total of 40 molecules of the same species were put in a box with controlled conditions, such as temperature and dimensions, and allowed to collide and react over some amount of time, over which the amounts of each species can be observed [11]. In this study, ReaxFF simulations were only done on GVL, in a cubical box with side length 32 Å. The system was equilibrated for 2.5ps at 1500K, and then continued

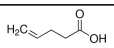
to run at 2000K [12].

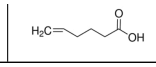
3 Results and Discussion

3.1 Measured YSIs

Measured YSIs for each lactone are listed in Table 1. The YSI of isooctane being 64.9 matched previously recorded values for the compound, indicating that the measurements were working properly. Uncertainties for measured YSIs presented in Table 1 refer to errors reflected in our repeated measurements. An error of ± 5.0 would take elements of systematic error, such as uncertainties in reported densities in literature or uncertainties in flow rate calculations and settings, into account. These lactones have low sooting tendencies, ranging from 17.2 to 45.2, compared to diesel's YSI of 256.1. This confirms the findings of Bereczky et al., that using lactones as fuel additives can suppress soot formation in exhaust [6].

Table 1: Name, abbreviation, structure, and predicted and measured YSIs for the endpoints, internal standard, 8 lactones, and 2 alkenoic acids; n-heptane and toluene do not have error ranges because they are the YSI scaling endpoints, and therefore have set, constant YSIs

Name	Abbr.	Structure	Measured YSI	Predicted YSI
n-heptane	HEP		36.0	36.0
toluene	TOL		170.9	170.9
isooctane	ISO		64.9 ± 0.5	61.7 ± 2.0
γ-butyrolactone	GBL		17.2 ± 0.9	11.0 ± 17.1
γ-valerolactone	GVL		34.9 ± 1.8	19.0 ± 16.9
γ-caprolactone	GCL		41.0 ± 2.1	25.6 ± 16.8
γ-heptanolactone	GHL		45.2 ± 1.5	32.2 ± 16.8
δ-valerolactone	DVL		21.1 ± 1.1	18.4 ± 17.1
δ-caprolactone	DCL		34.4 ± 1.7	26.3 ± 16.9
ϵ-caprolactone	ECL		36.2 ± 1.8	25.7 ± 17.1
α-Angelica lactone	AAL		28.7 ± 1.4	20.9 ± 17.2
4-pentenoic acid	4PA		37.3 ± 1.0	32.6 ± 9.2

5-hexenoic acid	5HA		37.2 ± 0.8	39.1 ± 9.2

3.2 Structure-Property Relationships

A molecule with a higher carbon number will intrinsically have a higher sooting tendency than others of its same species (assuming the sooting tendency measures soot per mole of dopant, which YSI does), because soot is made of carbon. Fig. 3 plots the measured YSI against carbon number for each lactone. As the carbon number increases from 4 to 7, the distribution of measured YSIs shifts upwards, confirming the aforementioned correlation. The distribution of YSIs at any carbon number is mainly due to the effects of varied chemical structures.

The main focus of this study is on the effects of those varied chemical structures on the sooting tendency of lactones. Specifically, the lactones' chemical structure will vary along the aforementioned degrees of freedom, which are the presence and length of side chains, ring size, and the presence of double bonds in the ring.

The effects of side chain presence and length can be observed from the γ- and δ- lactone series: The addition of a methyl group on GBL to form GVL increases the YSI by 17.7. Similarly, adding a methyl group onto DVL to form DCL increases YSI by 13.3. However, increasing the length of the side chain beyond 1 carbon, as seen from GVL, GCL, and GHL, increases YSI by 6.1 and 4.2, suggesting that the presence of the side chain is a much more significant factor in soot formation than length of the side chain.

The effect of ring size can be observed from GBL, DVL, and ECL, as well as from GVL and DCL. Interestingly, for the former, YSI increases with ring size, but for the latter, there is a negative correlation. Likewise, there does not seem to be a systematic trend for whether a carbon moving from the side chain to the ring increases or decreases sooting.

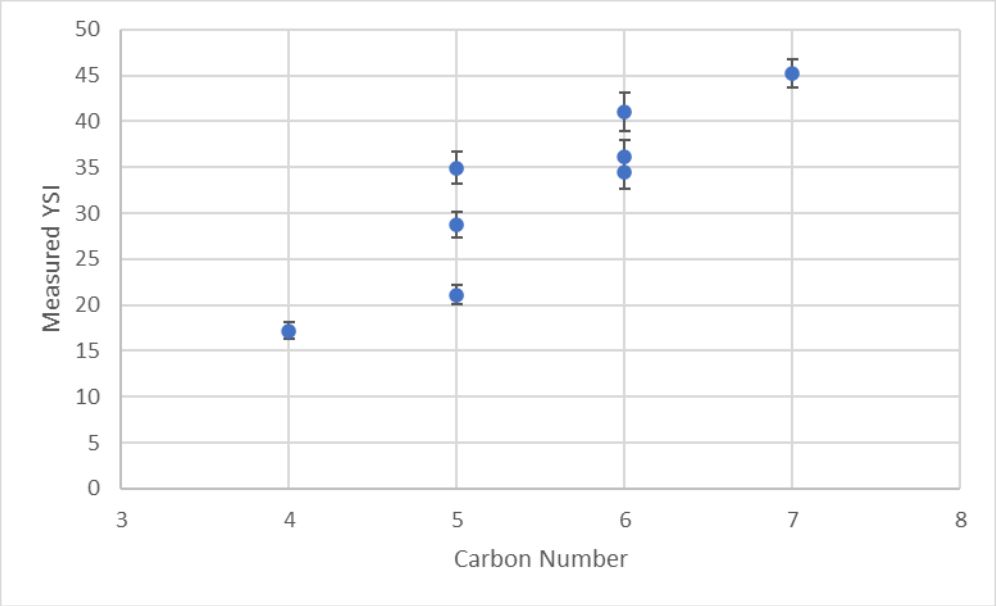


Figure 3: Measured YSI plotted against carbon number for each lactone.

Finally, comparing GVL and AAL, it seems that introducing a double bond into the ring suppresses sooting for lactones, which contrasts with previous observations done on species such as alkanes, where double bonds in rings increases YSI by promoting formation of benzene, an aromatic molecule that is a major precursor to soot formation. This result also contradicts the GCM prediction, which was that the YSI of AAL would be lower than that of GVL by 6.2. The reason for this contradiction is not yet well understood.

3.3 Comparison with Predictions

Fig. 4 is a graph comparing predicted and measured YSI values for the 8 lactones. Though the measured values were within error range for predictions, the predicted values were systematically lower than measured values. Though this is an intrinsic weakness of such a generalized (600+ compounds of various species) predictive model, giving the same model a specialized training set of lactones and similar compounds could result in a more accurate, albeit less generally applicable, model. However, the prediction error bars were very large due to small amounts of training data for a few of the lactones' functional groups. One possible explanation for the discrepancy between predicted and measured values is that the two oxygens on each lactone sequester the same carbon. The presence of oxygen usually serves to

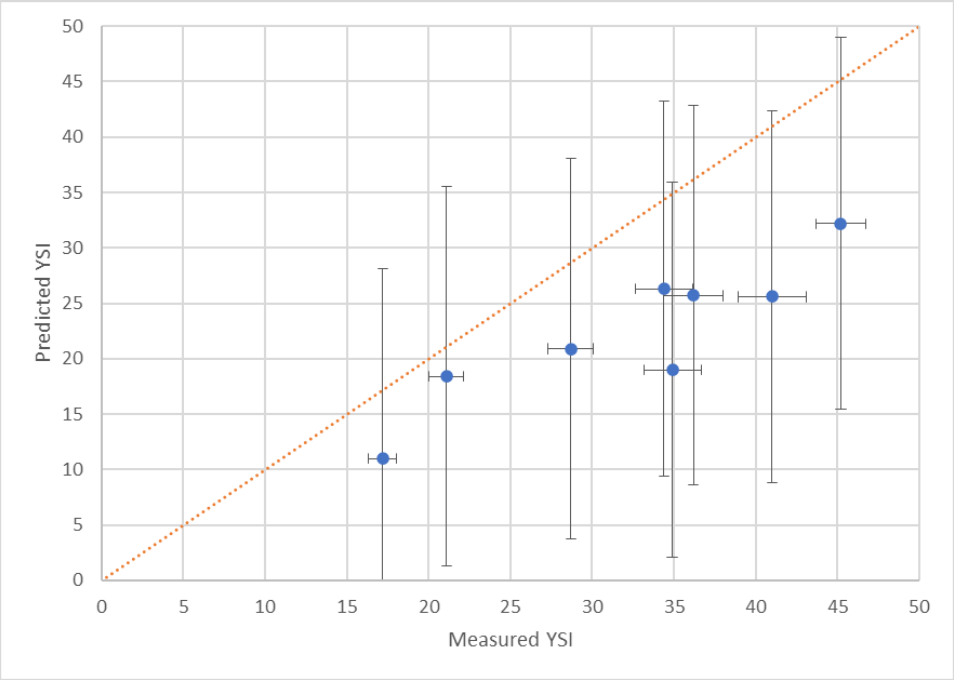


Figure 4: Predicted vs. measured YSI for the 8 studied lactones. A y=x line is shown in orange.

suppress soot formation, since oxygens bonded to carbons can eventually form CO_2, which removes that carbon from all soot formation processes, thereby reducing the total amount of soot formed. This inefficient use of oxygen means only one CO_2 is produced, increasing the number of available soot carbons, and therefore increasing the soot yield. This pathway is supported by ReaxFF simulations [12], that indicate that the dominant reaction for GVL is $C_5H_8O_2 \rightarrow C_4H_8 + CO_2$.

Given that oxygen functionality tends to decrease YSI, the estimator may have taken that sooting suppression affect into account for not just the carbon bonded to both oxygens, but also the other carbon single bonded to the oxygen in the ring, estimating a lower YSI contribution from that carbon even though the ring oxygen would have only sequestered that one carbon bonded to both oxygens.

3.4 Comparison with Alkenoic Acids

The ring opening product of both GVL (YSI = 34.9) and DVL (21.1) is 4PA (37.3), and the product of both ECL (36.2) and DCL (34.4) is 5HA (37.2). Aside from the case of DVL, the remaining three pairs of lactones and alkenoic acids seem to have similar enough YSIs so that such a ring opening reaction is plausible. It makes sense that the YSI of the alkenoic acids is slightly higher, since the additional step from lactone to alkenoic acid would delay soot formation to a higher point in the flame, decreasing the amount of soot at the set height in the flame where LSSR data is being recorded.

3.5 Future Directions

As the 8 lactones tested in this study were only a small sample meant to investigate possible structure-property relationships, a logical next step would be to confirm those relationships through testing of more lactones. This would also increase the amount of relevant training data in the training set for the YSI estimator, allowing it to give more accurate predictions in the future. Further molecular dynamics simulations could also help in determining dominant pathways for lactones other than GVL, giving insight into why those structure-property relationships exist.

Our preliminary measurements for the alkenoic acids showed that ring opening reactions from GVL to 4PA, DCL to 5HA, and ECL to 5HA are possible first steps in the soot formation pathways for those three lactones. Further testing of alkenoic acids, such as 3-butenoic acid (from GBL) and 4-hexenoic acid (from GCL, and as another possible product of DCL), would be necessary to confirm the existence of pathways presented by De Bruycker et al. [7]

4 Conclusions

This study was the first to characterize the sooting tendencies of 8 lactones with a single sooting index in a consistent setting, providing insight into possible novel structure-property relationships. The sooting index used to quantify the lactones' sooting tendencies in this

study was the yield sooting index, a relative scale based on the soot yield as measured in a nonpremixed methane/nitrogen coflow flame doped with each compound. The lactones' YSIs were low, ranging from 17.2 to 45.2, suggesting that they have potential as environmentally friendly fuel additives.

By comparing similar lactones' structures and YSIs, it is possible to predict structure-property relationships between YSI and side chain length, ring size, or double bond presence: Side chain length positively correlated with YSI, but its presence increased sooting much more than increasing its length. Ring size and YSI did not seem to have any consistent relationship. The presence of double bonds in the ring slightly decreased YSI, in the case of GVL and AAL, which was unexpected given the opposite effect in cyclic alkanes, and also disagreed with GCM predictions.

References

[1] Richard Burnett et al. Global estimates of mortality associated with long-term exposure to outdoor fine particulate matter. *PNAS*, 115:9592–9597, 2018.

[2] Christiane Voigt et al. Cleaner burning aviation fuels can reduce contrail cloudiness. *Communications Earth Environment*, 2, 2021.

[3] T. C. Bond et al. Bounding the role of black carbon in the climate system: A scientific assessment. *Journal of Geophysical Research: Atmospheres*, 118:5380–5552, 2013.

[4] ASTM. Standard test method for smoke point of kerosene and aviation turbine fuel. *ASTM*, 2019.

[5] Lisa D. Pfefferle Charles D. McEnally. Improved sooting tendency measurements for aromatic hydrocarbons and their implications for naphthalene formation pathways. *Combustion and Flame*, 148:210–222, 2007.

[6] Ákos Bereczky et al. Effect of -valerolactone blending on engine performance, combustion characteristics and exhaust emissions in a diesel engine. *Natural Resources*, 5:177–191, 2014.

[7] Ruben De Bruycker et al. An experimental and kinetic modeling study of -valerolactone pyrolysis. *Combustion and Flame*, 164:183–200, 2016.

[8] J. Gau et al. Yale coflow burner information and cad drawings. `https://figshare.com/articles/dataset/Yale_Coflow_Burner_Information_and_CAD_Drawings/5005007/1`, 2017.

[9] Zhanhong Xiang et al. Sooting tendencies of phenolic hydrocarbons. *Spring Technical Meeting, Eastern States Section of the Combustion Institute*, 37:911–918, 2022.

[10] Online ysi estimator. `https://ysi.ml.nrel.gov/`.

[11] Hyunguk Kwon et al. Reaxff-based molecular dynamics study of bio-derived polycyclic alkanes as potential alternative jet fuels. *Fuel*, 279, 2020.

[12] Yuan Xuan Ga-Un Jeong. Research in progress, 2023. Penn State University.