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Prediction of FID response factor of pyrolysis bio-oil components by effective carbon number model

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ABSTRACT

The analytical characterization of pyrolysis bio-oil represents a formidable challenge, attributed to its complex composition and inherent corrosive properties. Addressing this, we introduce an improved version of Effective Carbon Number (ECN) model, a novel predictive framework designed to accurately estimate the Flame Ionization Detector (FID) response factors of oxygenated compounds within bio-oil based solely on their molecular structures. The ECN model, underpinned by an analysis of over 150 compounds, leverages the structural attributes of molecules to ascertain their respective response factors, thereby facilitating precise concentration measurements. Central to our findings is the model's ability to correlate FID detector responses directly with two critical parameters: the total number of carbon atoms within the molecule, and the degree of oxidation of each carbon atom. Additionally, we have compiled a comprehensive table delineating response factors across various oxygenated functionalities, a resource that significantly expedites the analysis process of complex bio-oil mixtures.

Introduction

The transformation of lignocellulosic biomass into valuable chemicals and fuels stands as both a significant challenge and a crucial opportunity in reducing dependence on fossil fuels and advancing toward global sustainability goals [1-3]. Pyrolysis, coupled with catalytic upgrading, presents as a prevalent and cost-effective method for this transformation [3-6]. Pyrolysis involves the thermal decomposition of biomass in an oxygen-free environment at high temperatures, yielding a complex mixture of several hundred oxygenated compounds. The composition of the produced bio-oil, which typically varies in oxygen content from 20 to 50 wt.%, is highly dependent on the biomass source and pyrolysis conditions [4,7,8]. Such variability not only highlights the complex nature of bio-oil but also presents analytical challenges in consistently assessing its quality and composition before and after upgrading processes.

Various analytical techniques such as fractionation, gas chromatography, liquid chromatography, spectroscopy... have been employed in the study of bio-oil

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composition [6,9,10]. This research specifically emphasizes the use of gas chromatography (GC) coupled with Mass Spectrometry (MS) and Flame Ionization Detector (FID) to achieve comprehensive identification and quantification of compounds. The selection of GC-MS and GC-FID is motivated by their operational simplicity and heightened sensitivity to organic molecules. FID, in particular, is favored for quantitative analysis due to its linear response across a wide concentration range [11]. Crucially, the relative response of different compounds detected by FID is predominantly influenced by the chemical nature of the compounds themselves, rather than by the operational parameters of the device, allowing the development of a model capable of predicting the FID response of any given compound, based on its chemical nature [11-15].

The Response Factor (RF), linking FID response to compound concentration, is typically determined using commercial standards. This method, however, is not feasible for bio-oil analysis due to its complex composition and the lack of commercial availability for many of its constituents. A model to predict RF of FID is thus much needed for practical uses. Efforts to create such models have utilized a range of descriptors, from directly measurable, such as the number of C atoms that is only bonded to H, to those requiring computational methods like Gaussian simulations or DFT for complex properties like molecular repulsion energy or combustion enthalpy [16-20].

The Effective Carbon Number (ECN) model presents a more efficient method to directly estimate the RF based on a compound's structure. Initially introduced by Sternberg et al., this model assigns a specific response value to each carbon atom within a compound [21]. For example, carbon atoms in hydrocarbons like alkanes, alkenes, aromatics, or polycyclic aromatics are assigned a response value of approximately 1. In contrast, oxygenated carbon atoms exhibit a response value of less than 1. While Sternberg *et al.* provided ECN values for various carbon types, common bio-oil constituents such as furanics and functional phenolics were not covered [21-24]. This research aims to refine the ECN model to encompass all major bio-oil component families, particularly furanic and phenolic family, thereby enhancing its applicablity for comprehensive bio-oil analysis.

Experimental

Materials

Chemicals used in this study are purchased from Sigma Aldrich, with details as included in Supplemental Information.

GC configurations and method

In this research, for the analysis of bio-oil, we exclusively use column DB-1701 with column dimensions of 60 m x 0.25 mm and film thickness of 0.25 µm. Two different kinds of detectors were used, flame ionization detector (FID) and mass spectrometric (MS), in which the MS was used for identification and FID was used for quantification.

The gas chromatography (GC) analysis was conducted using an Agilent 6890 system equipped with an autosampler for injection. The inlet system featured a split injector, set at an injection temperature of 275°C for mass spectrometry (MS) and 200°C for the Flame Ionization Detector (FID), with a split ratio of 50. The oven temperature program began at 45°C, held for 2 minutes, followed by a ramp of 3°C/min to 280°C, where it was then maintained for 20 minutes. The injection volume for the analysis was set at 1 µL.

Effective Carbon Number (ECN), Response Factor (RF) and Relative Response Factor (RRF)

The Effective Carbon Number (ECN) concept was first introduced by Sternberg et al. as in Equation (1), with ECN is defaulted to be 7 for *n*-heptane [21].

$$\mathrm{ECN} = 7 * \frac{(\text{Peak area ration, sample to } n-\text{heptane})}{(\text{mole ratio, sample to } n-\text{heptane})} \quad (1)$$

Dietz et al. used weight to define the FID response factor of compound i (RF_i) as below [25].

$$\mathrm{RF_i} = \frac{\mathrm{A_i}}{\mathrm{m_i}} \quad (2)$$

$$\mathrm{RRF_{i/ref}} = \frac{\mathrm{RF_i}}{\mathrm{RF_{ref}}} \quad (3)$$

It is also useful in many cases to use the molar response factor (mRF) and molar relative response factor (mRRF), which is calculated based on the molar concentration [12,16], as following.

$$\mathrm{mRF_i} = \frac{\mathrm{A_i}}{\mathrm{C_{M,i}}} \quad (4)$$

$$\mathrm{mRRF_{i/ref}} = \frac{\mathrm{mRF_i}}{\mathrm{mRF_{ref}}} \quad (5)$$

The ECN thus can also be calculated based on mRRF as following.

$$\mathrm{ECN_i} = 7 * \mathrm{mRRF_{i/}}_{n-\mathrm{heptane}} \quad (6)$$

Where: RF_i : response factor of compound **i**

A_i : the peak area of compound i from GC-FID

m_i : mass of compound **i** in the sample

$C_{M,i}$:molar concentration of i in the sample

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Data collection and processing

The $RRF_{i/ref}$ values are predominantly determined by the chemical nature of the molecules (compound i and the reference) rather than the set up configuration of the GC. In fact, the RRF collected from 3 different sources have shown very good agreement with each others with deviation in the range of 0-8%, but mostly below 5% [8,17,25].

Therefore, the modified ECN model in this current study is further developed from existing ECN model of Sternberg et al. [21] using RRF of total 154 compounds, where we ultilize the published values from 3 different sources (summarized in Table S1) [8,17,25] in combination with our own experimental mRRF of 35 compounds (Table 1). In this databased of 154 compounds, there are 10 acid, 18 alcohol, 20 ketone/aldehyde, 11 ester, 25 hydrocarbons, 14 aromatic hydrocarbons, 49 phenolic and 9 sugar derived furanic molecules.

Linear regression of model fitting is done by minimizing the sum of square difference between the reported values and the predicted values.

Experimental mRRF

The experimental RRF in this study is determined for 35 different molecules using standard compounds purchased from Sigma-Aldrich and phenol is chosen as the reference molecules. The molar response factor mRF_i of each compound is determined based on the average values of 4 different molar concentrations using Equation (4), with the peak area is the area of FID signal (GC-FID configurations as specified in section 2b).

Results and discussion

Analysis approach for real bio-oil

As previously discussed, analyzing complex mixtures such as pyrolysis bio-oil necessitates a robust approach. This study employs GC-MS for qualitative analysis and GC-FID for quantitative assessments. To validate this methodology, we conducted a retention time comparison using model compounds selected from three primary chemical families typical in real bio-oil: light oxygenates (including acids and ketones), sugar-derived furanics, and lignin-derived phenolics.
These tests were carried out on two distinct sets of GC-MS and GC-FID equipment. The results confirmed a strong correspondence in retention times across the equipment, indicating reliable reproducibility and accuracy in our analytical approach. This consistency is clearly illustrated in Figure 1, which maps out the retention times for each of the model compounds, showcasing their good alignment.

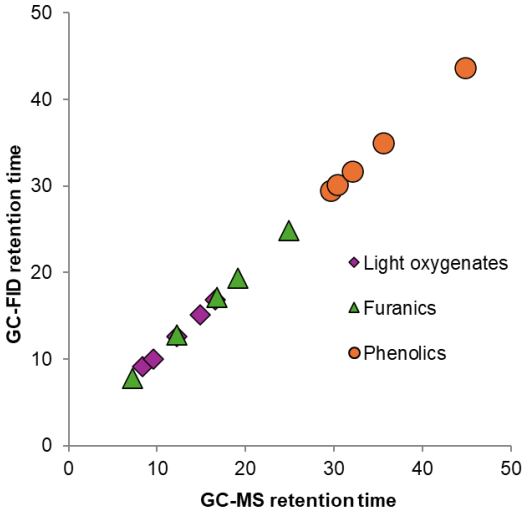

Fig. 1: Retention time from MS vs. FID of model compounds

When a real sample of a bio-oil fraction is injected through the column, the spectrums from both detectors also align well (Figure 2). This alignment reinforces the effectiveness of using GC-MS and GC-FID in tandem for the comprehensive analysis of pyrolysis bio-oil.

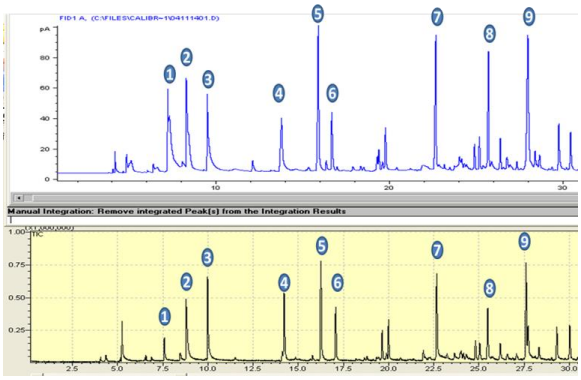

Fig. 2: Chromatogram profile of FID (top) and MS (bottom) of the same bio-oil sample.

The identification of each component was based on the library search available in the GC-MS analysis program. However, due to the complicated nature of bio-oil components, this library use is not always reliable and the identification process also needs to be further confirmed with the MS fragments of bio-oil compounds that have been previously reported from Faix and Meier et al. [10,26-28].

Experimental mRRF

Experimental mRRF values of 35 compounds where phenol is used as the reference are reported in Table 1.

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Table 1: Experimental mRRF values

Name	$mRRF_{i/phenol}$
Phenol	1
Anisole	1.07
m-Cresol	1.24
p-Cresol	1.04
2-Ethyl phenol	1.55
4-Ethyl phenol	1.19
2,5-Dimethoxy toluene	1.38
3,4,5-Trimethoxy toluene	1.65
Eugenol	1.60
1-Indanone	1.58
2-Ethoxy phenol	1.17
4-Ethoxy phenol	1.26
3,4-Dimethoxy toluene	1.27
3,5-Dimethoxy toluene	1.19
4-Ethyl guaiacol	1.34
2-Allyl phenol	1.30
2-Methoxy-4-propyl phenol	1.68
3-Isopropyl phenol	1.44
2-Methoxy-4-methyl phenol	1.12
2-Methyl anisole	1.06
4-Methyl anisole	1.06
3-Methyl anisole	1.03
2-Allyl-6-methyl phenol	1.72
2,3,5-Trimethyl phenol	1.57
2,4-Dimethylphenol	1.47
2,6-Dimethoxyphenol	1.32
Guaiacol	1.00
2'-Hydroxy-4'-methylacetophenone	1.22
m-Tolyl acetate	1.22
Acetic acid	0.14
Propionic acid	0.26
Butyric acid	0.55
Isobutyric acid	0.46
Acetol	0.16
Furfural	0.51
3,4-Dihydropyran	0.52

To reconfirm the validity of the assumption that the RRF, mRRF and ECN values do not depend on the GC set up or equipment configuration, but rather the nature of the chemical compounds, the $mRRF_{i/phenol}$ is compare between this study and the RRF values reported from Meier et al. [8]. The comparison is done on 11 chemical compounds that are from 3 main chemical families of bio-oil, light oxygenates, furanics and phenolics.

The response factor values reported by Meier et al. [8] used fluoranthene as the reference compound, which can be easily converted to mRRF with phenol as the reference using the Equation S1. The parity plot as shown in Figure 3 has indicated a very good agreement between mRRF values of different sources, proving the assumption that RRF, mRRF and ECN would depend predominantly on the nature of the chemical compounds. The details of chemical compounds and corresponding mRRF are included in Table S2.

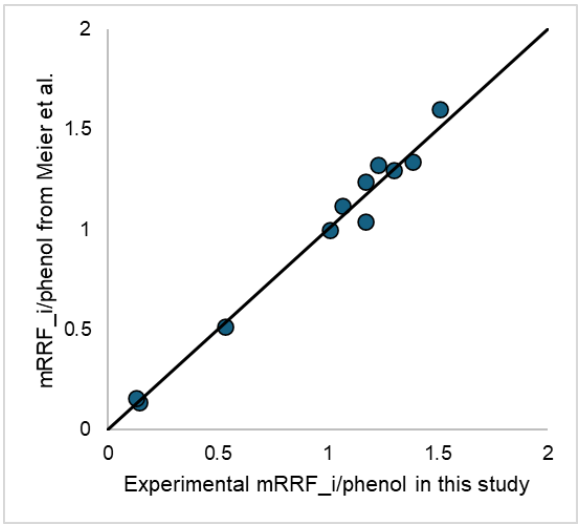

Fig. 3: Parity plot of $mRRF_{i/phenol}$ comparison between this study and Meier et al.[8]

ECN model

From our model optimization, the contribution to ECN value for different types of carbon are reported in Table 2 below. This table also shows how this new model is further improved from Sternberg's ECN model [21].

Based on Table 2, the ECN value can be easily predicted for any compound as long as its structure is known. For example, m-cresol has 6 aromatic C, 1 C attach to aromatic ring and 1 O of hydroxy on aromatic ring. Therefore, the ECN of m-cresol would be 6 x 1 + 1 x 0.6 – 1 x 0.75 = 5.85.

It is noteworthy that ECN value of any particular compound would never be negative. However, in Table 2, the ECN contribution could be negative since the oxidized carbon can also affect the ability generate FID signal of other carbon atoms in the molecule. Any compound that generate ECN of negative value based on this model will be considered ECN of zero. Compound such as formic acid or formaldehyde in fact have very insignificant RF values.

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Table 2: ECN contribution for different type of C

Atom	Type	ECN contribution	
		Sternberg	This study
C	Aliphatic	1	1
C	Aromatic	1	1
C	Olefinic	0.95	0.95
C	Attached to aromatic ring	N/A	0.6
C	Carbonyl	0	N/A
O	Carbonyl	N/A	-1
O	Ether	-1	-1
O	Ether in a ring	-1	-1.3
O	Ether attached to aromatic ring	-1	-1.1
O	Primary alcohol	-0.6	-0.56
O	Secondary alcohol	-0.75	-0.75
O	Tertiary alcohol	-0.25	-0.25
O	Ester	-0.25	-1.55
O	Carboxylic acid	N/A	-1.23
O	Hydroxy on aromatic ring	N/A	-0.75

As shown in Table 2, ECN contribution of aliphatic C, aromatic C and olefinic C are the same for both models. A significant improvement of this study's model is from assigning ECN contribution for C attaching directly to aromatic ring of 0.6. The model fittings of Aromatic hydrocarbon (HC) and phenolics families are significantly improved compared with Sternberg's.

Additionally, carbonyl group C=O is also evaluated differently. Since it has been observed that carbonyl group attached at different position will have different FID response, therefore our model proposes to use O in the carbonyl instead of C like in Sternberg's. This use of carbonyl O can account for the specific position of the carbonyl group.

Regarding ether -O- functionality, Sternberg's model has only 1 value for ether. However, with phenolics and furanics families, ether in a ring (i.e. furanics) or ether attached to aromatic ring (i.e. anisole and derivatives) will result in different FID response. Therefore the model also have different ECN contribution for different types of ether functionalities.

The ECN of alcohol is almost the same, this study's model proposed a slightly different value for O in primary alcohol, which is -0.56 instead of -0.6, while the secondary and tertiary alcohol O are the same.

Another big improvement of this study's model is in the contribution of ester, carboxylic acid and hydroxy on aromatic ring, which Sternberg's model did not capture. The model fitting for acid, ester, phenolics and furanics have shown significant enhancements.

The overall goodness of this new ECN model is demonstrated in Figure 4 a-b, where Figure 4a shows the parity plot of Sternberg's model and Figure 4b shows the ones of this study.

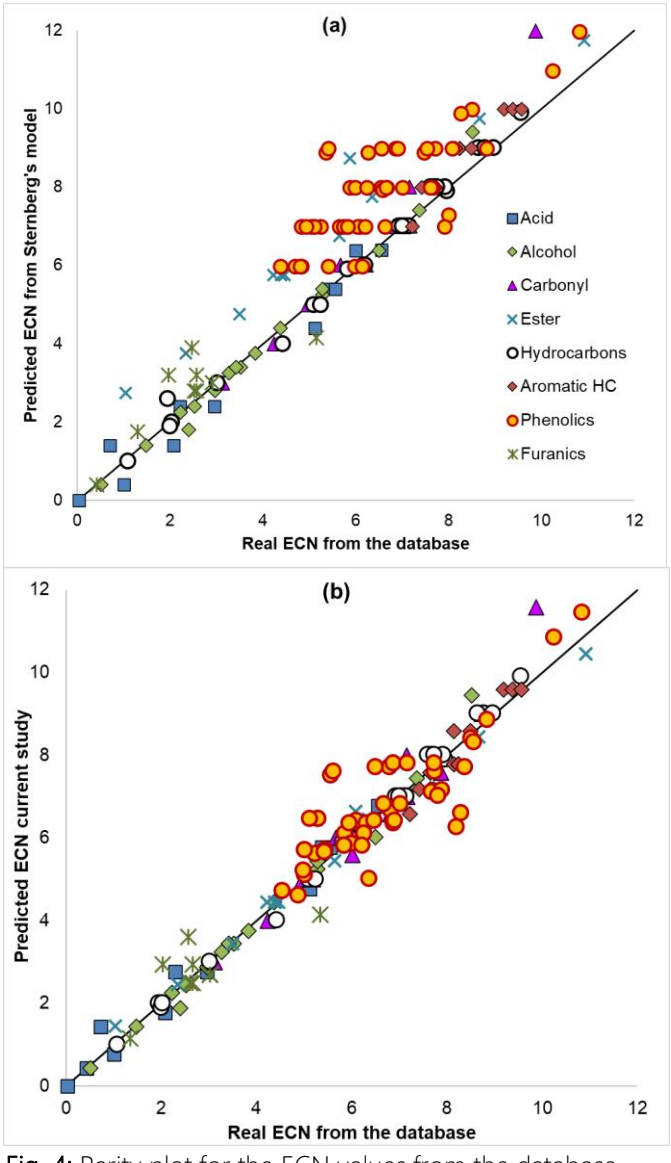

Fig. 4: Parity plot for the ECN values from the database vs. the predicted values from model of (a) Sternberg's and (b) this current study.

From the parity plots above, it could be seen that the current model works well with simple functionalities such as acid, alcohols, carbonyls, ester and

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hydrocarbons. The biggest deviations belong to furanic and phenolic families, in which the difference could be as high as 20-30% in some cases.

In pyrolysis bio-oil, furan derivatives are usually not stable and polymerization can happen during storage time; therefore, the reported values of the RF for furanics will have larger errors compared with other stable molecules. This experimental error cannot be captured in this model.

In phenolic family, 71% compounds have good model fitting with less than 10% deviation and 12% that do not fit the model well with deviation of 20-30%. The biggest deviations arises from syringol and its derivatives. Many oxygen containing functionalities present on aromatic ring at once may have different effects on ECN that this model has not been able to capture yet.

For further illustration of the effect of different functional groups on the ECN contributions, the ECN values were plotted against the number of carbons in the molecule as shown below.

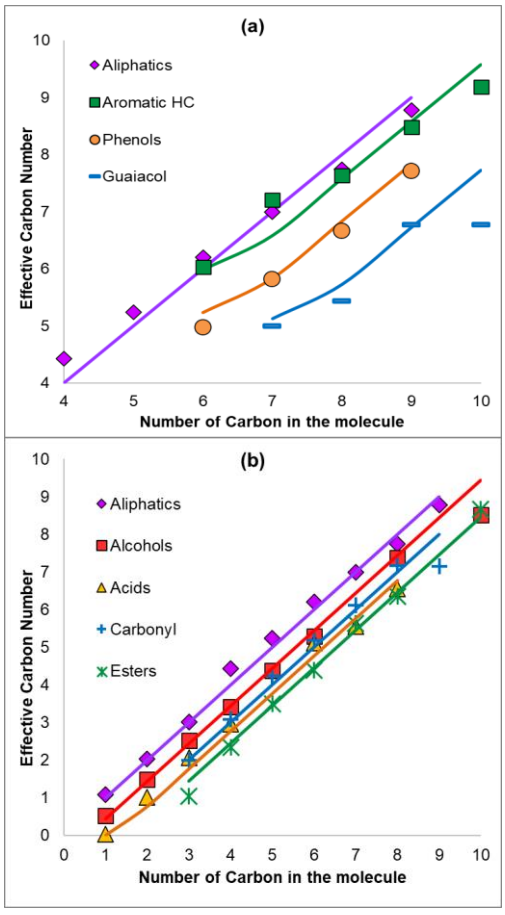

Fig. 5: ECN vs number of carbon in the molecules. The real values are represented by the markers and the predicted ECN models are solid lines of the same color

Conclusion

Bio-oil, characterized by its complex, unstable, and corrosive composition of oxygenated compounds, poses significant challenges for component quantification. This study demonstrates that accurate quantification is achievable using gas chromatography-mass spectrometry (GC-MS) for compound identification and gas chromatography-flame ionization detection (GC-FID) for quantification. The study has successfully developed an accessible and effective Effective Carbon Number (ECN) model that accurately predicts the response factors of compounds within bio-oil. The advancements offered by this ECN model hold substantial practical implications, extending beyond bio-oil to the analysis of other complex, naturally derived mixtures, potentially revolutionizing the approach to their study and utilization.
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References

1. D.E. Resasco, S. Crossley, AIChE Journal 55 (2009) 1082. https://doi.org/10.1002/aic.11893
2. D. Mohan, C.U. Pittman, Jr., P.H. Steele, Energy & Fuels 20 (2006) 848. https://doi.org/10.1021/ef0502397
3. J.A. Herron, T. Vann, N. Duong, D.E. Resasco, S. Crossley, L.L. Lobban, C.T. Maravelias, Energy Technology 5 (2017) 130. https://doi.org/10.1002/ente.201600147
4. H. Wang, J. Male, Y. Wang, ACS Catalysis 3 (2013) 1047. https://doi.org/10.1021/cs400069z
5. J. Wildschut, F.H. Mahfud, R. Venderbosch, H.J. Heeres, Industrial & Engineering Chemistry Research 48 (2009) 10324. https://doi.org/10.1021/IE9006003
6. E. Butler, G. Devlin, D. Meier, K. McDonnell, Renewable and Sustainable Energy Reviews 15 (2011) 4171. https://doi.org/10.1016/j.rser.2011.07.035
7. A.V. Bridgwater, Biomass and Bioenergy 38 (2012) 68. https://doi.org/10.1016/j.biombioe.2011.01.048
8. D. Meier, A. Oasmaa, C. Peacocke, 1997, 391-408. https://doi.org/10.1007/978-94-009-1559-6_31

9. M. Djokic, M. Dijkmans, G. Yildiz, W. Prins, K. Van Geem, Journal of chromatography. A 1257 (2012) 131. https://doi.org/10.1016/j.chroma.2012.07.035
10. D. Meier, O. Faix, Bioresource Technology 68 (1999) 71. https://doi.org/10.1016/S0960-8524(98)00086-8
11. K. Schofield, Progress in Energy and Combustion Science 34 (2008) 330. https://doi.org/10.1016/j.pecs.2007.08.001
12. J.Y. de Saint Laumer, S. Leocata, E. Tissot, L. Baroux, D.M. Kampf, P. Merle, A. Boschung, M. Seyfried, A. Chaintreau, Journal of separation science 38 (2015) 3209. https://doi.org/10.1002/jssc.201500106
13. S.S. Jacobsen, C.C. Becker, G. Hølmer, Chemometrics and Intelligent Laboratory Systems 23 (1994) 231. https://doi.org/10.1016/0169-7439(93)E0073-D
14. D. Singh, A. Chopra, R. Kumar, M.I.S. Sastry, M.B. Patel, B. Basu, Chromatographia 77 (2014) 165. https://doi.org/10.1007/s10337-013-2589-1
15. E. Cicchetti, P. Merle, A. Chaintreau, Flavour and Fragrance Journal 23 (2008) 450. https://doi.org/10.1002/ffj.1906
16. J.-Y. de Saint Laumer, E. Cicchetti, P. Merle, J. Egger, A. Chaintreau, Analytical Chemistry 82 (2010) 6457. https://doi.org/10.1021/ac1006574
17. A.R. Katritzky, E.S. Ignatchenko, R.A. Barcock, V.S. Lobanov, M. Karelson, Analytical Chemistry 66 (1994) 1799. https://doi.org/10.1021/ac00083a005
18. N. Kretzschmar, M. Seifert, O. Busse, J.J. Weigand, Data 7 (2022) 133. https://doi.org/10.3390/data7090133
19. E. Tissot, S. Rochat, C. Debonneville, A. Chaintreau, Flavour and Fragrance Journal 27 (2012) 290. https://doi.org/10.1002/ffj.3098
20. C. Cao, P. Huo, J Chromatogr Sci 45 (2007) 360. https://doi.org/10.1093/chromsci/45.6.360
21. W.S.G. J.C. Sternberg, D.T.L. Jones, in: J.E.C. N. Brenner, M.D. Weiss (Ed.), Gas Chromatography, New York, NY, Academic Press, 1962, 231.
22. A.D. Jorgensen, K.C. Picel, V.C. Stamoudis, Analytical Chemistry 62 (1990) 683. https://doi.org/10.1021/ac00206a007
23. F.W. Jones, Journal of Chromatographic Science 36 (1998) 223. 10.1093/chromsci/36.5.223
24. B. Lučlć, N. Trinajstić, S. Sild, M. Karelson, A.R. Katritzky, Journal of Chemical Information and Computer Sciences 39 (1999) 610. https://doi.org/10.1021/ci980161a
25. W.A. Dietz, Journal of Chromatographic Science 5 (1967) 68-71. https://doi.org/10.1093/chromsci/5.2.68
26. O. Faix, I. Fortmann, J. Bremer, D. Meier, Holz als Roh- und Werkstoff 49 (1991) 299-304. https://doi.org/10.1007/BF02663795
27. O. Faix, D. Meier, I. Fortmann, Holz als Roh- und Werkstoff 48 (1990) 351-354. https://doi.org/10.1007/BF02639897
28. O. Faix, I. Fortmann, J. Bremer, D. Meier, Holz als Roh- und Werkstoff 49 (1991) 213. https://doi.org/10.1007/BF02613278