

Highlights

- An equation for the change in energy quality presented
- Energy yield is shown to be a function of the change in energy quality and mass yield
- These energy metrics make cross-field comparisons of biofuels possible
- Increases in energy quality must be accompanied by decreases in mass yield

Energy metrics of fuel juxtaposed with mass yield metrics

Ryan D. Merckel,^{*a} Frederick J.W.J. Labuschagne,^a and Michael D. Heydenrych^{**a}

^a Department of Chemical Engineering, University of Pretoria, Private Bag X20, Hatfield, 0028, Pretoria, South Africa.

Corresponding Authors

*Correspondence: ryan.merckel@up.ac.za

**Correspondence: mike.heydenrych@up.ac.za

ABSTRACT

Without oxygen, there would be no combustion. Yet the crucial role of oxygen in energy systems has been largely underrepresented. The oxygen-dependence of fuel calorificity is used to derive energy-based metrics that challenge the prime facie objective of maximising biofuel mass yields—an objective that currently dominates the biofuel industry. Application of two energy metrics, namely the change in energy quality (ΔE_Q) and the energy yield (ΔE_η), demonstrates that any improvement in energy quality of combustibles must accompany increases in combusted oxygen (m_{O_2}), as $\Delta E_Q =$

$$\frac{m_{O_2}|_{\text{product}}}{m_{O_2}|_{\text{feed}}} - 1, \text{ and that } \Delta E_\eta \text{ is a function mass yield, } \eta, \text{ and } m_{O_2}; \Delta E_\eta = \eta \left(\frac{m_{O_2}|_{\text{product}}}{m_{O_2}|_{\text{feed}}} \right).$$

Literature data produced mostly positive ΔE_Q values: biocrude achieved the highest (126.3 %), followed by bioethanol (107.7 %), and catalytic pyrolysis (78.3 %). Most data produced similar changes in energy yield per mass yield, $\Delta E_\eta / \Delta m_\eta$ ranging from 0.7 for

biodiesel to 1.6 for bioethanol. Carbon yields and overall mass yields are demonstrated to be poor metrics for biofuel synthesis, and could undermine biofuel quality, hampering progress for conversion technologies aimed at producing biofuels. Biodiesel mass yields in particular were found to be inflated by as much as 73 %. As such, ΔE_Q and ΔE_η are useful for cross-field comparison of biofuels.

Keywords: Biofuels, energy quality, oxygen, higher heating value, mass yield, energy yield

1. Introduction

The valorisation of biomass to biofuel is characterized by alterations to chemical constituency, energy content and physical properties, and optimization of these alterations is central to the development of more sustainable energy products. It is well-known that during biofuel synthesis, deoxygenation can lead to a more energy-rich product, usually via the three main upgradation pathways of decarboxylation, dehydration and decarbonylation to produce CO_2 , H_2O and CO as by-products, respectively. The correlation of calorific value with fuel composition is also well-established, with the first example dating back to Dulong's association formula of 1880, as discussed by Gumz[1]. Dulong's formula associates the mass percentage for each of the major fuel elements of coal to the higher heating value ($\Delta_c h^\circ|_{\text{HHV}}$), as $\Delta_c h^\circ|_{\text{HHV}} = 81m_C + 25m_S - 290(m_H - m_O/8) - 6m_{\text{H}_2\text{O}}$ (MJ kg^{-1}) (mass of carbon = m_C , sulphur = m_S , hydrogen = m_H , and oxygen = m_O) and moisture ($m_{\text{H}_2\text{O}}$). Although not universally applicable to all types of conventional fuel, Dulong's formula nonetheless

provided some useful insights (particularly for lignite), resulted in a number of similar correlations being proposed, and is still used today. Subsequently, there now exists an abundance of correlations for estimating calorific values to suit any or all types of fuel[2]. Although not explicitly stated, the underlying premise of these correlations seems to imply that fuel elements ($C_{vC}, H_{vH}, O_{vO}, N_{vN}, S_{vS}$, etc.) are the *primary energy carriers* of combustion reactions. Unsurprisingly, only three attempts to correlate $\Delta_c h^\circ|_{\text{HHV}}$ solely with the oxygen required for combustion are known by the authors of this work. Both Rohr-Smidt[3] and Dietenberger[4] demonstrate that the energy liberated per quanta of oxygen consumed is more or less a constant ratio, while Rohr-Smidt provides a hypothesis that combustion exothermicity is consequence to the weak bonding of diatomic oxygen relative to combustion products. Only Merckel *et al.*[2] provide a theoretical derivation using bond dissociation enthalpy calculations to demonstrate definitively that the change in enthalpy undergone by oxygen is dominantly exothermic, and why the heat of combustion is a strong function of this exothermicity. This is epitomized in the accurate equation for $\Delta_c h^\circ|_{\text{HHV}}$ of

$$\Delta_c h^\circ|_{\text{HHV}} = \frac{x_{\text{O}_2}}{1 - x_{\text{O}_2}} \left[\frac{1 - x_{\text{O}_2}}{x_{\text{O}_2}} [\Delta_c D_H^*(\text{fuel}) + \Phi_c] + \frac{1 - x_{\text{O}_2}}{x_{\text{O}_2}} \Delta_c D_H(\text{O}_2) \right] - \Delta_c D_{H,m}(\text{H} \cdots \text{O}) + \Delta_{\text{RS}} h^\circ \quad (1)$$

where terms are specifically arranged merely for the purposes of simplifications that follow. It was previously shown by Merckel *et al.* that $\Delta_c h^\circ|_{\text{HHV}}$ is only a weak function of bond dissociation enthalpies and other energy associations with respect to the fuel (i.e., $\frac{1-x_{\text{O}_2}}{x_{\text{O}_2}} [\Delta_c D_H^*(\text{fuel}) + \Phi_c]$), as well as hydrogen bonding ($\Delta_c D_{H,m}(\text{H} \cdots \text{O})$) and resonance

energies ($\Delta_{RS}h^\circ$). Consequently, Equation 1 reduces to the less complex but still accurate form of [5]

$$\Delta_c h^\circ|_{\text{HHV}} = -13.87 m_{\text{O}_2} \quad (2)$$

which implies that $\Delta_c h^\circ|_{\text{HHV}}$ is a strong function of the mass of oxygen being combusted (m_{O_2}) per mass of fuel (m_{fuel}), and confirms Rohr-Smidt's own correlation. Equation 2 is applicable for a wide range of gaseous, liquid and solid fuels, with a root-mean-square error of just 1.5 MJ kg^{-1} and a coefficient of determination of $R^2 = 0.98$ based on 1087 fuel combustion data [2]. It follows that diatomic oxygen, rather than the fuel elements, is the *primary energy carrier* responsible for the exothermicity of combustion reactions. What does this say about the development of biofuels and energy systems? It implies that fuels serve as modulators of energy evolved during combustion, and combustion processes that consume more oxygen are decidedly more exothermic. Therefore, as energy products, biofuels should be manufactured so as to enhance their oxidation potentials. However, there is no standard method to compare various biofuels in terms of their energy value, let alone on the basis of oxidation potential.

For instance, mass and energy balances for the production of both biodiesel and bioethanol are well-documented, yet there are extensive variations in how these balances are carried out and complicates comparisons between the two technologies. What is more is that biodiesel mass yields are not conventionally determined in the same way as that of bioethanol, since mass yields pertaining to the synthesis of the alcohol used as well as oil yields from oleaginous biomass are seldom factored into biodiesel yield calculations. Typical of mass balances for the production of biodiesel

(Table 1) show that using the conventional definition (i.e. $m_{\text{biodiesel}} m_{\text{oil}}^{-1}$) inflates biodiesel yields by 13 % on average (i.e. if the basis of $m_{\text{biodiesel}} (m_{\text{oil}} + m_{\text{alcohol}})^{-1}$ is used instead), and yields are 73 % higher still when not taking into account the neat oil yield from the oleaginous biomass and alcohol (i.e. $m_{\text{biodiesel}} (m_{\text{alcohol}} + m_{\text{biomass}})^{-1}$). On the other hand, the widely adopted energy ratio (defined as the ratio of the energy produced in the form of transportation fuel to the non-renewable primary energy consumed to produce the fuel) is used to evaluate the performance of bioethanol as a fuel uses conventional fuels as a reference point, rather than other biofuels. It is also complex in its determination and may result in significant variations, which can lead to contradictory conclusions[6]. On the other hand, biofuel technologies that utilize the entire biomass feedstock to produce biofuel, such as fast pyrolysis, hydrothermal liquefaction and gasification, tend to report mass and energy balances less cryptically—such that more objective comparisons between these technologies can be made.

Using the insights into what fundamentally makes combustion-based energy systems reliable suppliers of heat and power, this work sets out to define a set of simple yet convenient energy-based metrics as a set of equations useful for the cross-field comparison of various biofuels (refer to Figure 1 for an outline of the objectives and structure of this study). The application of these energy metrics, specifically the change in energy quality and energy yield, are validated using data from the literature, are easy to use, and are further substantiated for adoption in the initial design and synthesis of biofuel-based energy systems.

2. Derivation and application of energy metrics

2.1. Experimental procedures

The graphical representations of the change in energy quality as a function of the total mass yield (Figure 3) and carbon mass yield (Figure 4), as well as the energy yield as a function of mass yield (Figure 7) were developed using the pythonTM software. A matrix of biomass compositions on the mass basis were first generated, and excluded data sets that produced compositions that were higher in oxidation than the combustion products of carbon dioxide and water. Upgradation of biomass was simulated by removing oxygen via the routes of dehydration, decarboxylation, decarbonylation, or a combination of these, and using the resulting mass and energy data to compile new matrices for the change in energy quality and energy yield. A sub-sample of the applicable data sets was taken to limit the number of data in each set to 1 million data points.

2.2. Definition of the change in energy quality

The efficacy of biomass-to-energy conversion technologies depends on how much energy is carried over from the biomass feedstock to the biofuel. If this carrier-over results in an increase in the calorific value for the biofuel, then the quality of this biofuel as an energy storage medium is deemed to be better than its parent biomass, and *vice versa*. This change in energy quality, ΔE_Q , may be described mathematically as the difference in calorific value between the biofuel product ($\Delta_c h^\circ|_{\text{HHV},p}$) and biomass feedstock ($\Delta_c h^\circ|_{\text{HHV},f}$) relative to the $\Delta_c h^\circ|_{\text{HHV},f}$:

$$\Delta E_Q = \frac{\Delta_c h^\circ|_{\text{HHV},p} - \Delta_c h^\circ|_{\text{HHV},f}}{\Delta_c h^\circ|_{\text{HHV},f}} \quad (3)$$

Since Equation 2 is applicable to just about all conventional fuels, whether in the gaseous, liquid or solid phase, it can be used to simplify Equation 3 without changing its own general applicability:

$$\Delta E_Q = \frac{-13.87 (m_{\text{O}_2}|_p - m_{\text{O}_2}|_f)}{-13.87 m_{\text{O}_2}|_f} \quad (4)$$

$$\Delta E_Q = \frac{m_{\text{O}_2}|_p}{m_{\text{O}_2}|_f} - 1$$

Equation 4 specifies that any increase in oxidation potential achieved by biomass-to-biofuel technologies (irrespective of the means taken to accomplish this) would result in an increase in energy quality. It should be noted that while $\Delta_c h^\circ|_{\text{HHV}}$ may be directly measured using bomb calorimetry, the lower heating value ($\Delta_c h^\circ|_{\text{LHV}}$) is a calculated value, where the amount of latent heat of vapourisation for water vapour that formed during combustion is subtracted from the measured $\Delta_c h^\circ|_{\text{HHV}}$. This requires (the not easily determined) quantity of water vapour formed during combustion. Fortunately, a linear relationship is observed when plotting the $\Delta_c h^\circ|_{\text{HHV}}$ against the $\Delta_c h^\circ|_{\text{LHV}}$ for numerous gaseous, liquid and solid fuel (Figure S1) and the resulting correlation may be used for interchanges between the two definitions for heat of combustion. It also does not change the result of Equation 4 and Equation 5.

2.3. Properties of the change in energy quality

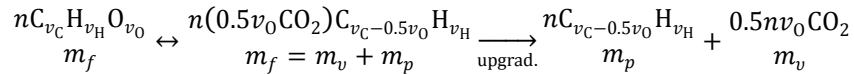
A graphical analysis of Equation 4 is presented in Figure 2 that explores how changes in energy quality may come about as a response to the primary deoxygenation-

dependant upgradation pathways of decarboxylation, dehydration, and decarbonylation. Figure 2A plots trendlines for biomass of varying oxygen content (solid lines) together with a hydrogen-free biomass composition (black dotted and dashed lines). The average composition for biomass obtained from the biomass data presented in Figure S1 is also provided as the reference point (green circle with black border) together with its respective upgradation trendlines (solid black lines). Biomass with higher initial oxygen content corresponds to more pronounced changes to energy quality while biomass of lower oxygen content does not respond to upgradation as much (Figure 2A). Where biomass is sufficiently low in oxygen content, the decarbonylation pathway results in an increase in ΔE_Q . But for biomass of higher oxygen content, a reduction in ΔE_Q occurs when decarbonylation is favoured in place of decarboxylation. The amount of carbon content in biomass also affects the response of ΔE_Q to decarbonylation for biomass. Biomass of varying amounts of oxygen, but high in carbon content, has a much sharper response to upgradation by decarbonylation (Figure 2B, solid purple lines), compared to biomass with lower carbon content (Figure 2B, solid green lines). Biomass deficient in hydrogen shows a dramatic reduction in mass yield following upgradation via the decarbonylation route (Figure 2A, dotted and dashed black lines), but the same change in energy quality is obtained regardless of whether upgradation proceeds via decarbonylation or decarboxylation. However, all biomass compositions analysed accordingly show no difference when compared by the decarboxylation and dehydration pathways and forms a boundary for upgradation (Figure 2A, solid dark red line; Figure 2C, dark red dashed line). The boundary limit for deoxygenation via dehydration is

obtained for a molar hydrogen-oxygen ratio (H:O) of 2:1 (i.e. the molecular formula for water) and is simply the dehydration curve.

These boundary limits become much clearer when plotting a very large amount of data for the total mass yield of some primary product(s) produced from the upgradation of some arbitrary C:H:O-containing feedstock(s) (Figure 2C, dark red dashed line). Using hypothetical biomass compositions of varying mass percentages of carbon, hydrogen and oxygen between 0 % and 100 %, the plot of Figure 3 is obtained and covers all practically possible biomass/biofuel compositions—those compositions that lie within an “unattainable” region are excluded (i.e. for degrees of oxidation that would not normally occur as a result of combustion). Irrespective of variations in biomass/feedstock composition, Figure 3 shows that any increase in energy quality must be accompanied by a decrease in the mass yield. Since oxygen content has a negative effect on energy quality and biomass invariably contains oxygen, the mass yield must be decreased in accordance to oxygen removal. The ratio of hydrogen to carbon in the product too must be adjusted accordingly to bring about changes in energy quality and will also contribute to a reduction in mass yield. This is because hydrogen ($\Delta_c h^\circ|_{\text{HHV}} = -141.8 \text{ MJ kg}^{-1}$ [66]) liberates much more energy during combustion than carbon ($\Delta_c h^\circ|_{\text{HHV}} = -32.8 \text{ MJ kg}^{-1}$ [66]), but is also much lighter than carbon per mole. Inevitably, the reduction in mass yield is required for upgrading via deoxygenation since the product must fall within the attainable region (bounded by the red curve of Figure 3). Therefore, it is not possible to increase the mass yield beyond a certain limit without negatively affecting the energy quality of the fuel being produced. All this is of course obvious, but is also very useful in identifying the mathematical

equation that defines the apparent boundary shown in Figure 2C and Figure 3. This boundary limit may be explained as the removal of mass through upgradation that would not in theory affect the quantity of combustion-related energy for the fuel in question. This upgradation mass may be represented by way of molecular rearrangement as follows:



where $nv_0\text{CO}_2$ (m_v) is some arbitrary non-combustible component of the biomass with molecular composition $n\text{C}_{v_c}\text{H}_{v_H}\text{O}_{v_0}$ (m_f), while $n\text{C}_{v_c-0.5v_0}\text{H}_{v_H}$ (m_p) represents the combustible component of the biomass. Although m_p may be much lighter than m_f and subsequently have a higher oxidation potential, energy content is preserved. Therefore, the energy of the feedstock is equal to the energy in the product: $\Delta_c h^\circ|_{m_f} \times m_f =$

$\Delta_c h^\circ|_{m_p} \times m_p$, and by application of Equation 2, $m_{\text{O}_2}|_{m_f} \times m_f = m_{\text{O}_2}|_{m_p} \times m_p$. If $m_{\text{O}_2} = \frac{m_{\text{O}_2}^*}{m_{\text{fuel}}}$

(where $m_{\text{O}_2}^*$ represents the amount of oxygen required to combust a certain mass of fuel

m_{fuel}), then $\frac{m_{\text{O}_2}^*|_{m_f}}{m_f} \times m_f = \frac{m_{\text{O}_2}^*|_{m_p}}{m_p} \times m_p$, which simplifies to $m_{\text{O}_2}^*|_{m_f} = m_{\text{O}_2}^*|_{m_p}$. By applying

this result to Equation 3, the following is obtained:

$$\Delta E_Q = \frac{m_{\text{O}_2}|_p}{m_{\text{O}_2}|_f} - 1 = \frac{m_{\text{O}_2}^*|_{m_p}/m_p}{m_{\text{O}_2}^*|_{m_f}/m_f} - 1$$

$$\Delta E_Q = \frac{m_f}{m_p} - 1 \quad 5$$

Despite being an ostensibly unremarkable equation, the properties of Equation 5 provide the strongest criticism against the objectives of maximizing the mass yields of

biofuels that have until now been used *prima facie*. The greatest increase in energy quality of a material intended for use as a fuel comes from the greatest decrease in redundant mass (i.e. energy-deficient mass removed through upgradation such as CO₂ or H₂O), where ΔE_Q approaches infinity when the upgradation mass m_v approaches the mass of the material undergoing upgradation ($m_v \rightarrow m_f$), or rather $m_p \rightarrow 0$:

$$\lim_{m_p \rightarrow 0} \Delta E_Q = \Delta E_Q|_{\text{limit}} = \lim_{m_p \rightarrow 0} \frac{m_f}{m_p} - 1 \rightarrow \infty$$

If no upgradation takes place (in other words, $m_v = 0$ and $m_p = m_f$), then there will be no change in energy quality:

$$\Delta E_Q|_{m_p=m_f} = \frac{m_f}{m_p}|_{m_p=m_f} - 1 = 0$$

Although energy evolution via the combustion reaction requires there to be some mass association and attaining this limit would be nonsensical, these limits nonetheless confirm the overall consistency of Equation 5.

2.4. The change in energy quality and carbon yield

Unlike for the total mass yield, the carbon yield does not exhibit a boundary of upgradation (Figure 4). It also cannot be concluded that maximising carbon yield will result in the highest change in energy quality—there is simply no trend in the data that would suggest this. More than 99.9% of the data shown in Figure 4, which is representative all possible feed compositions, correspond to a maximum change in energy quality of 116%. This implies that by achieving a favourable carbon yield in the upgraded product will not inevitably bring about the highest possible change in energy

quality. In general, a change of no more than 116 % can be expected—anything higher than this is more unlikely for most feedstock compositions. If the average biomass feedstock ($C_{1.00}H_{1.35}O_{0.65}$) is considered for upgradation to a fuel, the maximum possible change in energy quality obtained for a 100 % carbon yield is just $\Delta E_Q = 103 \%$, as shown in Table 2.

2.5. Definition of energy yield

While Equation 4 determines the change in energy quality when transforming biomass to a biofuel, it does not evaluate how much of the energy contained in the biomass actually reports to the biofuel. By applying Equation (2) again, the efficiency of preserving the biomass-derived energy in the biofuel may be determined as follows:

$$\Delta E_\eta = \frac{\Delta_c h^\circ |_{\text{HHV},p} \times m_p}{\Delta_c h^\circ |_{\text{HHV},f} \times m_f}$$

$$\Delta E_\eta = \frac{-13.87 m_{\text{O}_2}|_p \times m_p}{-13.87 m_{\text{O}_2}|_f \times m_f}$$

$$\Delta E_\eta = \eta \frac{m_{\text{O}_2}|_p}{m_{\text{O}_2}|_f} \tag{6}$$

where η is the mass yield and ΔE_η is the energy yield. According to Equation 6, energy yield is both a function of the mass yield, being directly proportional to it, and the change in energy quality via the relation $m_{\text{O}_2}|_p/m_{\text{O}_2}|_f$. Equation 6 implies that the highest energy yield is achieved by obtaining the highest possible change in energy quality *and* mass yield. Conversely, if mass yield was instead optimised, then, for any given energy yield, a reduction in energy quality would correspond to an increase in

mass yield — in the case of producing transportation fuels from biomass resources this is clearly not desired!

3. Application of energy metrics

The applicability of the change in energy quality (Figure 5) and energy yield (Figure 6) is demonstrated using literature data for biocrude[7–13], bioethanol[14–29], biodiesel[30–33] (with the change in energy quality reported on both a vegetable oil and a total biomass basis), as well as uncatalyzed[34–56] and catalysed[48,57–62] pyrolysis oil. It should be noted that only the primary products are considered when analysing the change in energy quality (Figure 5) and energy yield (Figure 6). By-products that have the potential to combust would of course contribute favourably towards energy metrics, but unnecessarily complicates the intention of the comparisons presented. Of the data analysed in this way, uncatalyzed fast pyrolysis resulted in pyrolysis oils with the widest variance with respect to the change in energy quality. Some data resulted in a negative change in energy quality (as low as -21.4%) while most other data resulted in a positive ΔE_Q , with the highest value of 103.1% being achieved. Biocrude data achieved the highest change in energy quality (126.3%), followed by bioethanol (107.7%). By comparison, catalytic fast pyrolysis resulted in less favourable changes in energy quality, ranging between -14.6% and 78.3% .

In contrast to the lack of any notable correlations for changes in the energy quality, the energy yields showed obvious trends for these same data. All the trendlines of Figure 6 exhibit similar changes in energy yield per mass yield, $\Delta E_\eta/\Delta m_\eta$, with values of 0.7 for biodiesel, 1.0 for both uncatalyzed fast pyrolysis and biocrude, 0.9 for catalysed

pyrolysis, and 1.6 ethanol. Close similarities in these gradients suggest that correlations between the energy yield and the mass yield is somewhat independent of the type of conversion technology being used. This seems to be contrary to what is suggested by the theoretical presentation of energy yield as a function of the mass yield of Figure 7. The correlations of Figure 6 do not necessarily advocate for lower mass yields as the causative agent in reductions of energy yields. As previously demonstrated by the data presented in Figure 7, it may be more indicative of a misdirection in how the optimisation of conversion technologies is being implemented, such as optimising for higher mass yields of a product.

For instance, the majority of literature data cited by this work was found to focus heavily on optimisation studies, in which correlations between temperature, residence times, and mass yields are presented with a strong emphasis on producing the highest mass yield. This is especially typical of fast pyrolysis[63–65] and biocrude[66] research that aim to achieve high oil yields and limit the production of biochar and non-condensable gases. Bioethanol technologies go a step further by optimising for higher fermentable sugar yields derived from biomass and targeting the highest conversions of these intermediates to bioethanol[67]. Biodiesel technologies are similar in that they too focus on optimising for triglyceride yields and their subsequent conversion to biodiesel[68,69]. This reasoning at least in part explains the scatter observed in the data of Figure 6, and why some technologies are able to obtain energy yields close of 90 % or more at mass yields of less than 50 % while others obtain less than 40 % in energy yield for similar mass yields. This variance reduces with a reduction in mass yield

obtained, and seems to converge as the mass yield approaches 0 %, and corresponding to an energy yield of 0%.

Whether it is practically possible for bioprocessing and biorefining technologies to achieve more favourable energy yields at lower mass yields still remains to be seen. What is certain is that energy metrics may very well impact the development and optimisation of energy systems, especially concerning energy storage and utilization.

4. Conclusions

Oxygen has been demonstrated previously to be the primary energy carrier responsible for the exothermicity of combustion reactions, irrespective of the phase or form of the fuel. A set of energy metrics have been derived from the resulting strong correlation between the calorific value of fuels and oxygen consumption, namely the change in energy quality and the energy yield. This set of energy metrics are used successfully to perform cross-field comparisons of various biofuels in terms of their energy value and oxidation potential. The change in energy quality is only a function of the ratio of oxygen consumption of the product to the feedstock, where an increase in oxidation potential of the product relative to the feedstock leads to a greater change in the energy quality. A maximum boundary limit in the change in energy quality exists and is found to be a function of the ratio between the mass of the feed to the product. Surprisingly, improvements in energy quality for biomass-to-biofuel conversions is only possible with decreases in the mass yield. Energy yield is proportional to both mass yield and the change in energy quality, where the highest energy yields are achieved through obtaining the highest mass yields and change in energy quality. The change in

energy quality and energy yield equations are applied to literature data for biocrude, bioethanol, biodiesel, uncatalysed and catalysed pyrolysis oil. No correlation is observed between the mass yield and the change in energy quality. Biocrude achieved the highest change in energy (126.3 %) followed by bioethanol (107.7 %), while pyrolysis oil showed the highest variance and obtained a negative change in energy quality in some instances. A linear correlation between energy yield and mass yield for the same data was observed and was found to be independent of the conversion technology.

The method of approach for design of sustainable biofuel processes requires a joint consideration from both the mass- and energy-based perspectives. Such considerations should incorporate cross-field comparisons with other biofuel processes and products so that more definitive and holistic deductions can be made. It is therefore recommended that the energy metrics presented in this study be (i) employed as a means of normalising such comparisons, and (ii) used as benchmarking tools for evaluating the competitiveness of biofuel processes and products.

ACKNOWLEDGMENTS

R.D.M. thanks Yun-Wen Wu and Maria M.M. de Wet for their assistance with editing the graphics presented in this work. The authors also acknowledge the continued financial support received from the Paper Manufacturers Association of South Africa (PAMSA).

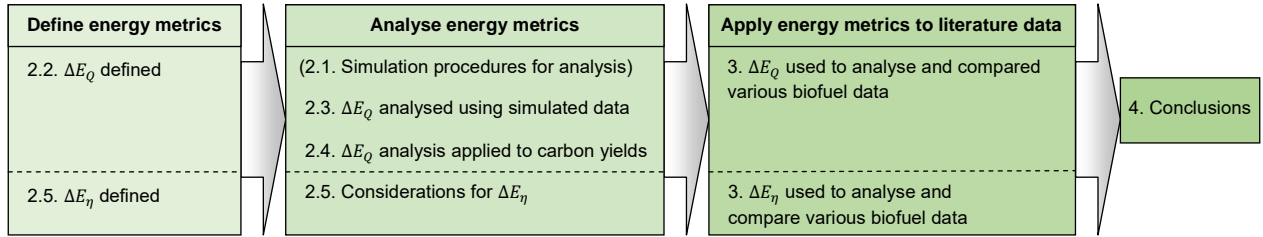


Figure 1. Objectives (boldface) and structure (numbered items) of this study.

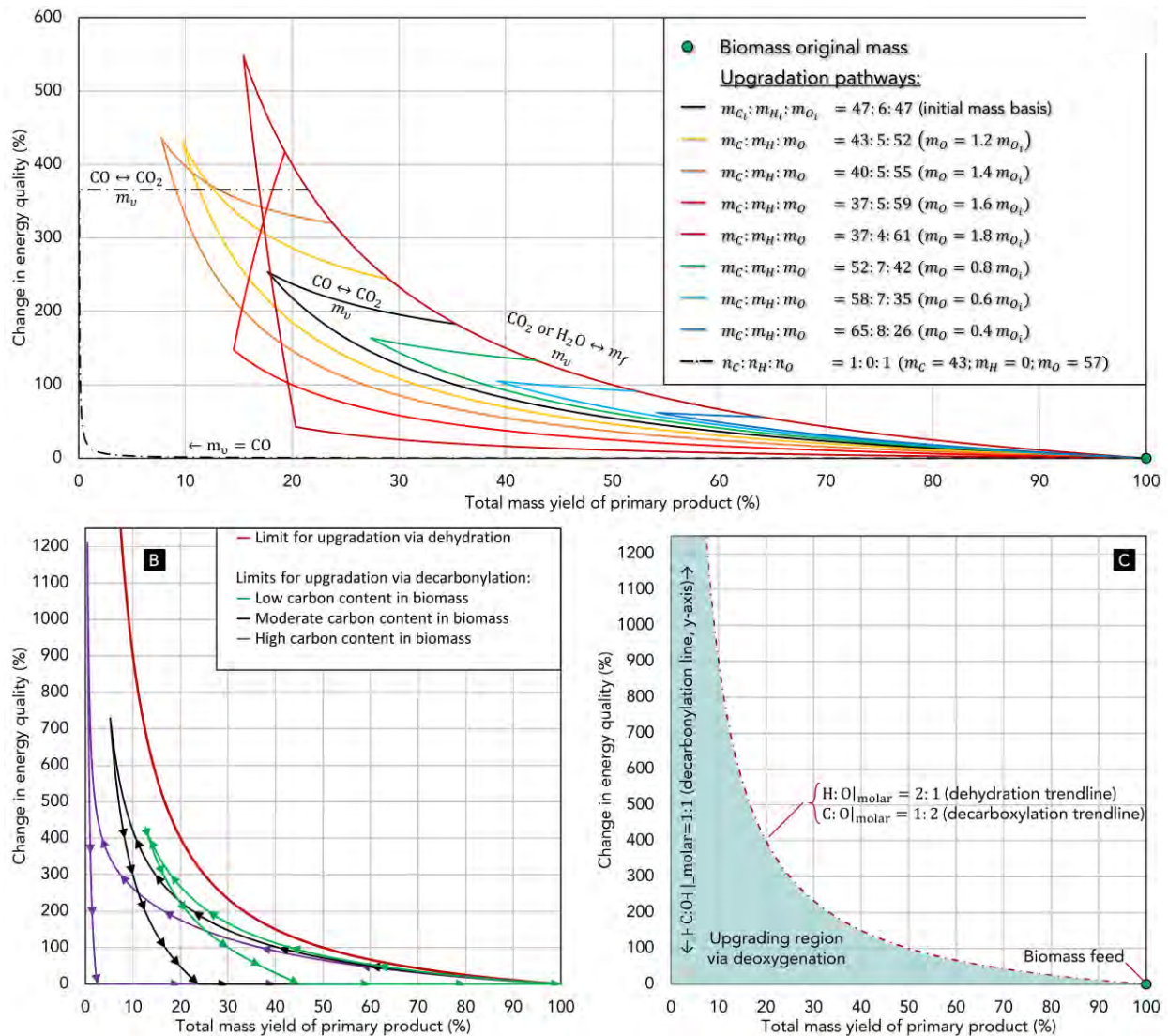


Figure 2. Boundaries of upgradation under varying initial elemental composition of biomass. (A) The sensitivity of biomass composition (green circle with black border) to upgradation is demonstrated, where the trendlines represent the pathway taken by the products of upgradation. (B) Variance in biomass oxygen composition on biomass accompanies variances in carbon content, and affects upgradation via decarbonylation: fuel produced from low carbon content biomass via decarbonylation achieves lower changes in energy quality (solid green lines) compared to biomass with carbon content that is moderate (black solid lines) and high (solid purple lines).

(C) Irrespective of biomass composition, the change in energy quality as a function of the mass yield is distinguished by a boundary line (red dotted and dashed line) that, theoretically, approach infinity for ΔE_Q as the mass yield approaches zero.

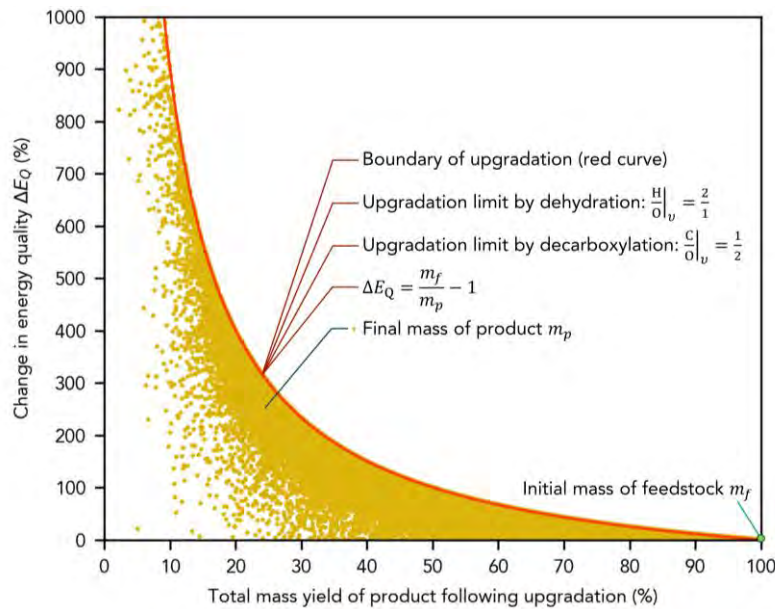


Figure 3. Total mass yield of the primary product plotted against the change in energy quality following upgradation of C:H:O-containing feedstock. Upgradation of biomass feedstock m_f to a primary energy product m_p is achieved by increasing the oxidation potential via the reaction pathways of dehydration, decarboxylation and decarbonylation. The increase in oxidation potential is directly related to an increase in energy quality, but is limited. This limit is a function of the ratio of the initial mass of feed and the final mass of product, and suggests that any positive change in the energy quality must accompany a reduction in the mass yield. This limit, referred to here as the boundary of upgradation, is associated with the dehydration and decarboxylation of the biomass.

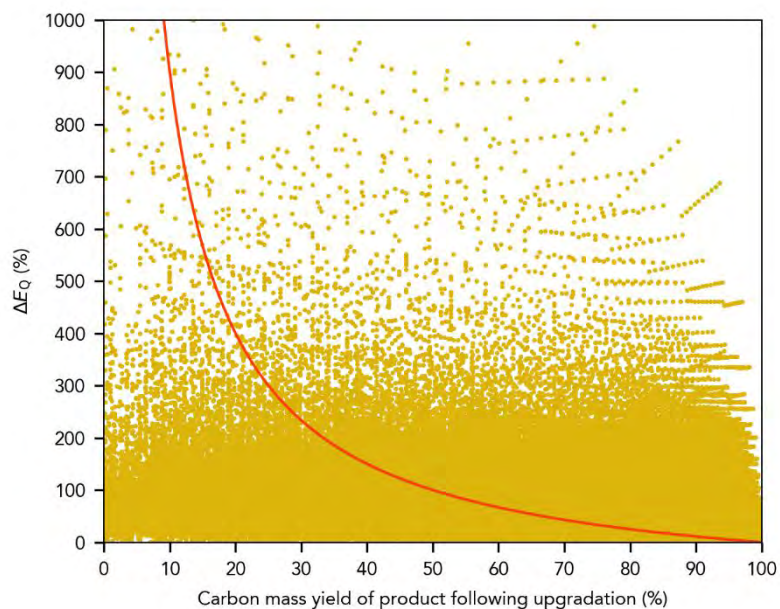


Figure 4. Total mass yield of the primary product plotted against the change in energy quality following upgradation of C:H:O-containing feedstock. A comparison of the change in energy quality and the carbon mass yield does not produce the same consequences of Figure 6. This suggests that carbon efficiency may not be related to the energy quality of biofuels at all, and using carbon efficiency as a criterion of evaluation for conversion processes might not lead to improvements in fuel properties.

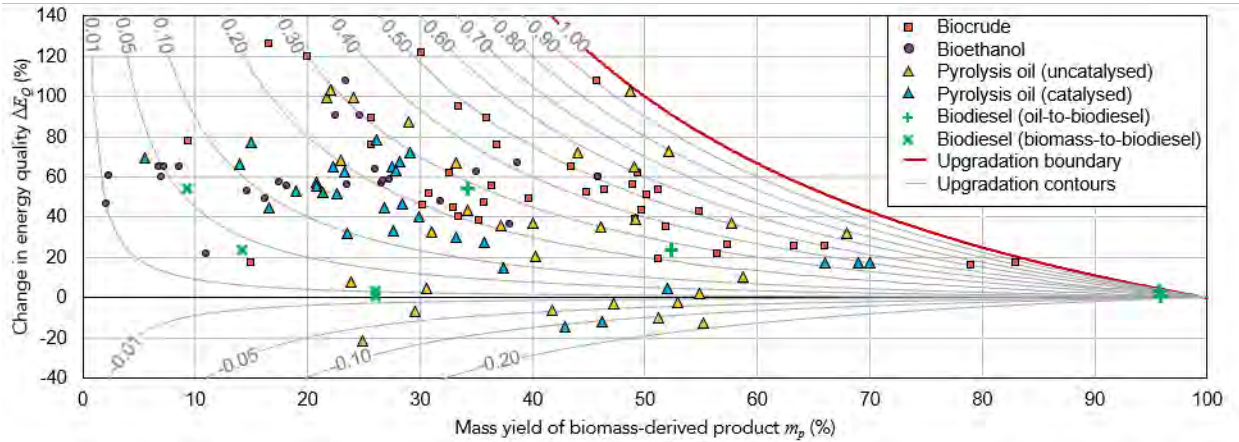


Figure 5. Total mass yield versus change in energy quality for data obtained from literature. The change in energy quality versus mass yield for data obtained in the literature for biocrude[7–13], bioethanol[14–29], biodiesel[30–33] as well as uncatalysed[34–56] and catalysed[48,57–62] pyrolysis oil as the primary products are compared. Also shown is the fraction of $\Delta E_Q|_{\text{limit}}$ as grey curves. No general trend is obvious, but most data does not achieve upgradation that is close to the boundary limit, apart from three datum for biocrude and one datum for pyrolysis oil. Most data achieve a positive change in energy quality, while some result in a negative change in energy quality: most are for uncatalysed pyrolysis oil, with two contributions from catalysed pyrolysis oil.

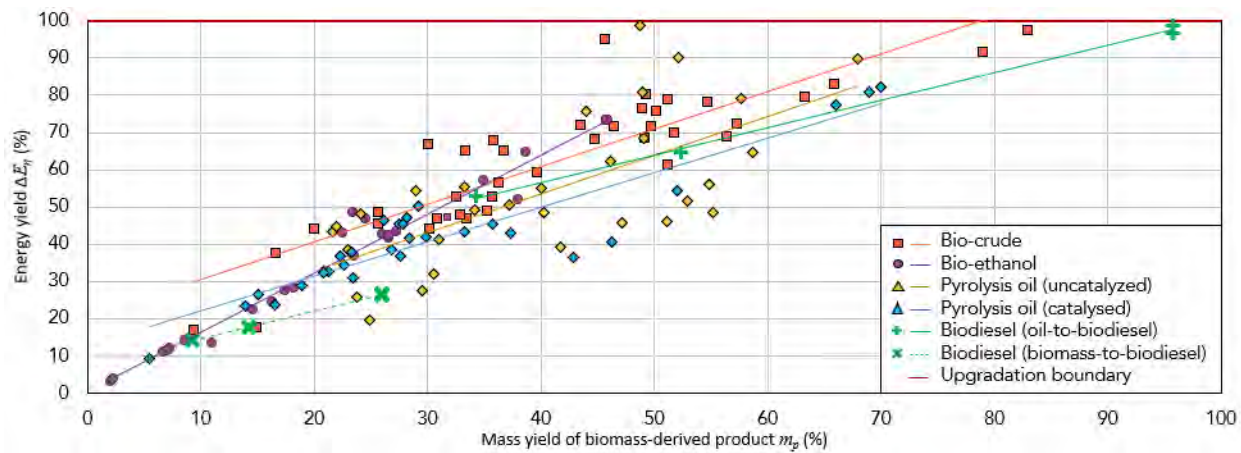


Figure 6. Total mass yield versus energy yield for data obtained from literature.

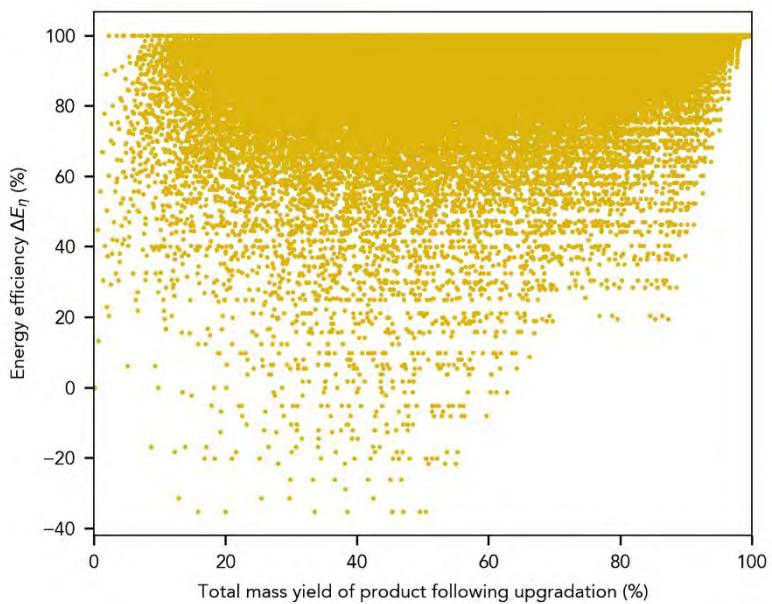


Figure 7. Total mass yield of the primary product plotted against the energy yield following upgradation of C:H:O-containing feedstock.

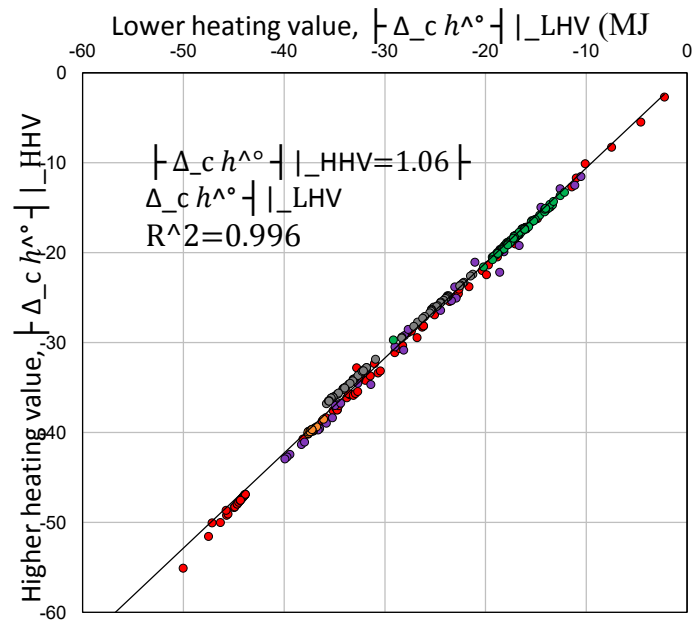


Figure S1. Plot of the higher heating value against the lower heating value. Note the linear correlation, for which there is not much deviation, despite data being presented for all types of gaseous, liquid and solid fuel.

Table 1. Summary of mass balances for biodiesel production

Biomass type	Mass yields (kg per 100 kg _{biomass} ⁻¹)				Biodiesel yield (%)			Ref.
	Alcohol	Neat oil	Glycerol	Biodiesel	Conventional basis ^a	Oil basis ^b	Total basis ^c	
Soybean (<i>Glycine max</i>)	2.7	17.4	1.8	17.0	98.3	84.5	16.6	[70]
Soybean (<i>Glycine max</i>)	2.8	20.0	2.1	18.7	93.5	82.0	18.2	[70]
Oil palm fruit (<i>Elaeis guineensis</i>)	2.5	19.3	3.1	18.3	95.2	84.4	17.9	[71]
Canola (<i>Brassica napas</i>)	4.8	34.1	3.6	32.5	95.3	83.6	31.0	[72]
Ethiopian mustard (<i>Brassica carinata</i>)	5.3	33.1	4.1	32.1	97.0	83.6	30.5	[73]
Averages:	3.6	24.8	2.9	23.7	95.7	83.6	22.8	

$$^a \eta_{\text{biodiesel}} \% = m_{\text{biodiesel}}/m_{\text{oil}} \times 100 \%$$

$$^b \eta_{\text{biodiesel}} \% = m_{\text{biodiesel}}/(m_{\text{oil}} + m_{\text{alcohol}}) \times 100 \%$$

$$^c \eta_{\text{biodiesel}} \% = m_{\text{biodiesel}}/(m_{\text{oil}} + m_{\text{alcohol}} + m_{\text{biomass}}) \times 100 \%$$

Table 2. Comparisons between mass and energy metrics for various biomass-to-biofuel scenarios

Deoxygenation routes ^a	$\Delta_c h^\circ$	E_η	ΔE_Q	Primary product yields	
	(MJ kg ⁻¹)	(%)	(%)	carbon (%)	total (%)
Not applicable: combustion only ^c	0.0	0	-100	100.0	233.6 ^d
via H ₂ O	-33.6 ^b	100	103	100.0	49.1
via CO ₂	-48.6	100	164	65.3	37.9
via CO	-58.1	66	215	30.5	20.9
89.3 % via CO ₂ , 10.7 % via CO	-49.2	96	167	61.4	36.0
40.3 % via CO ₂ , 57.1 % via H ₂ O	-40.1	100	118	86.0	45.9

^a The average biomass composition for data presented in Figure 2, with a molecular formula of C_{1.00}H_{1.48}O_{0.69}, is used

^b Calculated using individual $\Delta_c h^\circ$ values for carbon and hydrogen

^c Combustion is assumed to be complete, producing the products of CO₂ and H₂O

^d Includes oxygen consumed during combustion

REFERENCES

- [1] W. Gumz, Kurzes Handbuch der Brennstoff- und Feuerungstechnik, 2nd Edition, Springer-Verlag, Berlin, 1953.
- [2] R. Merckel, F. Labuschagne, M. Heydenrych, Oxygen as the definitive factor in predicting heat of combustion, *Applied Energy*. 235 (2019) 1041–1047.
<https://doi.org/10.1016/j.apenergy.2018.10.111>.
- [3] K. Schmidt-Rohr, Why Combustions Are Always Exothermic, Yielding About 418 kJ per Mole of O₂, *J. Chem. Educ.* 92 (2015) 2094–2099.
<https://doi.org/10.1021/acs.jchemed.5b00333>.
- [4] M. Dietenberger, Update for combustion properties of wood components, *Fire and Materials*. 26 (2002) 255–267. <https://doi.org/10.1002/fam.807>.
- [5] R. Merckel, F. Labuschagne, M. Heydenrych, Corrigendum to “Oxygen consumption as the definitive factor in predicting heat of combustion” [*Appl. Energy* 235 (2019) 1041-1047], 254 (2019) 1041–1047.
<https://doi.org/10.1016/j.apenergy.2019.113628>.
- [6] E. Gnansounou, A. Dauriat, ENERGY BALANCE OF BIOETHANOL: A SYNTHESIS, (n.d.) 5.
- [7] R. Shakya, S. Adhikari, R. Mahadevan, S.R. Shanmugam, H. Nam, E.B. Hassan, T.A. Dempster, Influence of biochemical composition during hydrothermal

- liquefaction of algae on product yields and fuel properties, *Bioresour. Technol.* 243 (2017) 1112–1120. <https://doi.org/10.1016/j.biortech.2017.07.046>.
- [8] H.S. Choi, Y.S. Choi, H.C. Park, The influence of fast pyrolysis condition on biocrude-oil yield and homogeneity, *Korean J. Chem. Eng.* 27 (2010) 1164–1169. <https://doi.org/10.1007/s11814-010-0213-8>.
- [9] N. Neveux, A.K.L. Yuen, C. Jazrawi, M. Magnusson, B.S. Haynes, A.F. Masters, A. Montoya, N.A. Paul, T. Maschmeyer, R. de Nys, Biocrude yield and productivity from the hydrothermal liquefaction of marine and freshwater green macroalgae, *Bioresour. Technol.* 155 (2014) 334–341. <https://doi.org/10.1016/j.biortech.2013.12.083>.
- [10] D.R. Vardon, B.K. Sharma, J. Scott, G. Yu, Z. Wang, L. Schideman, Y. Zhang, T.J. Strathmann, Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina* algae, swine manure, and digested anaerobic sludge, *Bioresource Technology.* 102 (2011) 8295–8303. <https://doi.org/10.1016/j.biortech.2011.06.041>.
- [11] F.A. Agblevor, S. Beis, S.S. Kim, R. Tarrant, N.O. Mante, Biocrude oils from the fast pyrolysis of poultry litter and hardwood, *Waste Manag.* 30 (2010) 298–307. <https://doi.org/10.1016/j.wasman.2009.09.042>.
- [12] X. Wang, B. Zhao, X. Yang, Co-pyrolysis of microalgae and sewage sludge: Biocrude assessment and char yield prediction, *Energy Conversion and Management.* 117 (2016) 326–334. <https://doi.org/10.1016/j.enconman.2016.03.013>.

- [13] P. Duan, P.E. Savage, Catalytic hydrotreatment of crude algal bio-oil in supercritical water, *Applied Catalysis B: Environmental*. 104 (2011) 136–143.
<https://doi.org/10.1016/j.apcatb.2011.02.020>.
- [14] E.M. de Medeiros, J.A. Posada, H. Noorman, P. Osseweijer, R.M. Filho, Hydrous bioethanol production from sugarcane bagasse via energy self-sufficient gasification-fermentation hybrid route: Simulation and financial analysis, *Journal of Cleaner Production*. 168 (2017) 1625–1635.
<https://doi.org/10.1016/j.jclepro.2017.01.165>.
- [15] A. Mishra, S. Ghosh, Bioethanol production from various lignocellulosic feedstocks by a novel “fractional hydrolysis” technique with different inorganic acids and co-culture fermentation, *Fuel*. 236 (2019) 544–553.
<https://doi.org/10.1016/j.fuel.2018.09.024>.
- [16] R. Muktham, A.S. Ball, S.K. Bhargava, S. Bankupalli, Bioethanol production from non-edible de-oiled *Pongamia pinnata* seed residue-optimization of acid hydrolysis followed by fermentation, *Industrial Crops and Products*. 94 (2016) 490–497.
<https://doi.org/10.1016/j.indcrop.2016.09.019>.
- [17] I.A. Sanusi, F.D. Faloye, E.B. Gueguim Kana, Impact of Various Metallic Oxide Nanoparticles on Ethanol Production by *Saccharomyces cerevisiae* BY4743: Screening, Kinetic Study and Validation on Potato Waste, *Catal Lett*. 149 (2019) 2015–2031. <https://doi.org/10.1007/s10562-019-02796-6>.

- [18] Y. Yuan, D.J. Macquarrie, Microwave Assisted Acid Hydrolysis of Brown Seaweed *Ascophyllum nodosum* for Bioethanol Production and Characterization of Alga Residue, *ACS Sustainable Chem. Eng.* 3 (2015) 1359–1365.
<https://doi.org/10.1021/acssuschemeng.5b00094>.
- [19] B.J. Khawla, M. Sameh, G. Imen, F. Donyes, G. Dhouha, E.G. Raoudha, N.-E. Oumèma, Potato peel as feedstock for bioethanol production: A comparison of acidic and enzymatic hydrolysis, *Industrial Crops and Products.* 52 (2014) 144–149. <https://doi.org/10.1016/j.indcrop.2013.10.025>.
- [20] S.-H. Ho, S.-W. Huang, C.-Y. Chen, T. Hasunuma, A. Kondo, J.-S. Chang, Bioethanol production using carbohydrate-rich microalgae biomass as feedstock, *Bioresour. Technol.* 135 (2013) 191–198.
<https://doi.org/10.1016/j.biortech.2012.10.015>.
- [21] G. Markou, I. Angelidaki, E. Nerantzis, D. Georgakakis, Bioethanol Production by Carbohydrate-Enriched Biomass of *Arthrospira (Spirulina) platensis*, *Energies.* 6 (2013) 3937–3950. <https://doi.org/10.3390/en6083937>.
- [22] O.K. Lee, A.L. Kim, D.H. Seong, C.G. Lee, Y.T. Jung, J.W. Lee, E.Y. Lee, Chemo-enzymatic saccharification and bioethanol fermentation of lipid-extracted residual biomass of the microalga, *Dunaliella tertiolecta*, *Bioresource Technology.* 132 (2013) 197–201. <https://doi.org/10.1016/j.biortech.2013.01.007>.
- [23] J.-S. Jang, Y. Cho, G.-T. Jeong, S.-K. Kim, Optimization of saccharification and ethanol production by simultaneous saccharification and fermentation (SSF) from

seaweed, *Saccharina japonica*, *Bioprocess Biosyst Eng.* 35 (2012) 11–18.

<https://doi.org/10.1007/s00449-011-0611-2>.

[24] S. Ewanick, R. Bura, The effect of biomass moisture content on bioethanol yields from steam pretreated switchgrass and sugarcane bagasse, *Bioresour. Technol.* 102 (2011) 2651–2658. <https://doi.org/10.1016/j.biortech.2010.10.117>.

[25] C. Muñoz, R. Mendonça, J. Baeza, A. Berlin, J. Saddler, J. Freer, Bioethanol production from bio-organosolv pulps of *Pinus radiata* and *Acacia dealbata*, *Journal of Chemical Technology & Biotechnology.* 82 (2007) 767–774. <https://doi.org/10.1002/jctb.1737>.

[26] M.G. Borines, R.L. de Leon, J.L. Cuello, Bioethanol production from the macroalgae *Sargassum* spp, *Bioresour. Technol.* 138 (2013) 22–29. <https://doi.org/10.1016/j.biortech.2013.03.108>.

[27] H.A. Ruiz, D.P. Silva, D.S. Ruzene, L.F. Lima, A.A. Vicente, J.A. Teixeira, Bioethanol production from hydrothermal pretreated wheat straw by a flocculating *Saccharomyces cerevisiae* strain – Effect of process conditions, *Fuel.* 95 (2012) 528–536. <https://doi.org/10.1016/j.fuel.2011.10.060>.

[28] M. Han, S.-K. Moon, Y. Kim, Y. Kim, B. Chung, G.-W. Choi, Bioethanol production from ammonia percolated wheat straw, *Biotechnol Bioproc E.* 14 (2009) 606. <https://doi.org/10.1007/s12257-008-0320-0>.

- [29] C. Lareo, M.D. Ferrari, M. Guigou, L. Fajardo, V. Larnaudie, M.B. Ramírez, J. Martínez-Garreiro, Evaluation of sweet potato for fuel bioethanol production: hydrolysis and fermentation, SpringerPlus. 2 (2013) 493.
<https://doi.org/10.1186/2193-1801-2-493>.
- [30] M. Anwar, M. Rasul, N. Ashwath, Optimization of biodiesel production from stone fruit kernel oil, Energy Procedia. 160 (2019) 268–276.
<https://doi.org/10.1016/j.egypro.2019.02.146>.
- [31] S.E. Onoji, SYNTHESIS OF BIODIESEL FROM RUBBER SEED OIL FOR INTERNAL COMPRESSION IGNITION ENGINE, University of the Witwatersrand, 2017.
- [32] M. Anwar, M.G. Rasul, N. Ashwath, M.M. Rahman, Optimisation of Second-Generation Biodiesel Production from Australian Native Stone Fruit Oil Using Response Surface Method, Energies. 11 (2018) 2566.
<https://doi.org/10.3390/en11102566>.
- [33] A.K. Yadav, A. Pal, A.M. Dubey, Experimental Studies on Utilization of Prunus armeniaca L. (Wild Apricot) Biodiesel as an Alternative Fuel for CI Engine, Waste Biomass Valor. 9 (2018) 1961–1969. <https://doi.org/10.1007/s12649-017-9935-8>.
- [34] J.P. Bok, H.S. Choi, Y.S. Choi, H.C. Park, S.J. Kim, Fast pyrolysis of coffee grounds: Characteristics of product yields and biocrude oil quality, Energy. 47 (2012) 17–24. <https://doi.org/10.1016/j.energy.2012.06.003>.

- [35] S.-J. Kim, S.-H. Jung, J.-S. Kim, Fast pyrolysis of palm kernel shells: influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds, *Bioresour. Technol.* 101 (2010) 9294–9300.
<https://doi.org/10.1016/j.biortech.2010.06.110>.
- [36] S. Şensöz, D. Angın, S. Yorgun, Influence of particle size on the pyrolysis of rapeseed (*Brassica napus* L.): fuel properties of bio-oil, *Biomass and Bioenergy*. 19 (2000) 271–279. [https://doi.org/10.1016/S0961-9534\(00\)00041-6](https://doi.org/10.1016/S0961-9534(00)00041-6).
- [37] R. Fahmi, A.V. Bridgwater, I. Donnison, N. Yates, J.M. Jones, The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability, *Fuel*. 87 (2008) 1230–1240. <https://doi.org/10.1016/j.fuel.2007.07.026>.
- [38] S. Yorgun, S. Şensöz, Ö.M. Koçkar, Characterization of the pyrolysis oil produced in the slow pyrolysis of sunflower-extracted bagasse, *Biomass and Bioenergy*. 20 (2001) 141–148. [https://doi.org/10.1016/S0961-9534\(00\)00064-7](https://doi.org/10.1016/S0961-9534(00)00064-7).
- [39] L. Li, H. Zhang, X. Zhuang, Pyrolysis of Waste Paper: Characterization and Composition of Pyrolysis Oil, *Energy Sources*. 27 (2005) 867–873.
<https://doi.org/10.1080/00908310490450872>.
- [40] S.H. Beis, Ö. Onay, Ö.M. Koçkar, Fixed-bed pyrolysis of safflower seed: influence of pyrolysis parameters on product yields and compositions, *Renewable Energy*. 26 (2002) 21–32. [https://doi.org/10.1016/S0960-1481\(01\)00109-4](https://doi.org/10.1016/S0960-1481(01)00109-4).

- [41] A.E. Pütün, Biomass to Bio-Oil via Fast Pyrolysis of Cotton Straw and Stalk, *Energy Sources*. 24 (2002) 275–285.
<https://doi.org/10.1080/009083102317243656>.
- [42] S. Şensöz, Slow pyrolysis of wood barks from *Pinus brutia* Ten. and product compositions, *Bioresource Technology*. 89 (2003) 307–311.
[https://doi.org/10.1016/S0960-8524\(03\)00059-2](https://doi.org/10.1016/S0960-8524(03)00059-2).
- [43] T. Cornelissen, J. Yperman, G. Reggers, S. Schreurs, R. Carleer, Flash co-pyrolysis of biomass with polylactic acid. Part 1: Influence on bio-oil yield and heating value, *Fuel*. 87 (2008) 1031–1041.
<https://doi.org/10.1016/j.fuel.2007.07.019>.
- [44] R. He, X.P. Ye, B.C. English, J.A. Satrio, Influence of pyrolysis condition on switchgrass bio-oil yield and physicochemical properties, *Bioresource Technology*. 100 (2009) 5305–5311. <https://doi.org/10.1016/j.biortech.2009.02.069>.
- [45] H.F. Gerçel, The production and evaluation of bio-oils from the pyrolysis of sunflower-oil cake, *Biomass and Bioenergy*. 23 (2002) 307–314.
[https://doi.org/10.1016/S0961-9534\(02\)00053-3](https://doi.org/10.1016/S0961-9534(02)00053-3).
- [46] N. Özbay, A.E. Pütün, B.B. Uzun, E. Pütün, Biocrude from biomass: pyrolysis of cottonseed cake, *Renewable Energy*. 24 (2001) 615–625.
[https://doi.org/10.1016/S0960-1481\(01\)00048-9](https://doi.org/10.1016/S0960-1481(01)00048-9).

- [47] J.-L. Zheng, Pyrolysis oil from fast pyrolysis of maize stalk, *Journal of Analytical and Applied Pyrolysis*. 83 (2008) 205–212.
<https://doi.org/10.1016/j.jaap.2008.08.005>.
- [48] F. Ateş, A.E. Pütün, E. Pütün, Fixed bed pyrolysis of *Euphorbia rigida* with different catalysts, *Energy Conversion and Management*. 46 (2005) 421–432.
<https://doi.org/10.1016/j.enconman.2004.03.011>.
- [49] A.E. Pütün, H.F. Gerçel, Ö.M. Koçkar, Ö. Ege, C.E. Snape, E. Pütün, Oil production from an arid-land plant: fixed-bed pyrolysis and hydrolysis of *Euphorbia rigida*, *Fuel*. 75 (1996) 1307–1312. [https://doi.org/10.1016/0016-2361\(96\)00098-1](https://doi.org/10.1016/0016-2361(96)00098-1).
- [50] F. TUNCEL, H.F. GERCEL, Production and Characterization of Pyrolysis Oils from *Euphorbia Macroclada*, *Energy Sources*. 26 (2004) 761–770.
<https://doi.org/10.1080/00908310490451394>.
- [51] M. Asadullah, M.A. Rahman, M.M. Ali, M.S. Rahman, M.A. Motin, M.B. Sultan, M.R. Alam, Production of bio-oil from fixed bed pyrolysis of bagasse, *Fuel*. 86 (2007) 2514–2520. <https://doi.org/10.1016/j.fuel.2007.02.007>.
- [52] C. Acikgoz, O. Onay, O.M. Kockar, Fast pyrolysis of linseed: product yields and compositions, *Journal of Analytical and Applied Pyrolysis*. 71 (2004) 417–429.
[https://doi.org/10.1016/S0165-2370\(03\)00124-4](https://doi.org/10.1016/S0165-2370(03)00124-4).

- [53] O. Onay, O. Mete Koçkar, Fixed-bed pyrolysis of rapeseed (*Brassica napus* L.), *Biomass and Bioenergy*. 26 (2004) 289–299. [https://doi.org/10.1016/S0961-9534\(03\)00123-5](https://doi.org/10.1016/S0961-9534(03)00123-5).
- [54] F. Ateş, E. Pütün, A.E. Pütün, Fast pyrolysis of sesame stalk: yields and structural analysis of bio-oil, *Journal of Analytical and Applied Pyrolysis*. 71 (2004) 779–790. <https://doi.org/10.1016/j.jaap.2003.11.001>.
- [55] H.F. Gerçel, Production and characterization of pyrolysis liquids from sunflower-pressed bagasse, *Bioresource Technology*. 85 (2002) 113–117. [https://doi.org/10.1016/S0960-8524\(02\)00101-3](https://doi.org/10.1016/S0960-8524(02)00101-3).
- [56] A.E. Pütün, N. Özbay, E.P. Önal, E. Pütün, Fixed-bed pyrolysis of cotton stalk for liquid and solid products, *Fuel Processing Technology*. 86 (2005) 1207–1219. <https://doi.org/10.1016/j.fuproc.2004.12.006>.
- [57] F. Ateş, M.A. Işıkdağ, Influence of temperature and alumina catalyst on pyrolysis of corncob, *Fuel*. 88 (2009) 1991–1997. <https://doi.org/10.1016/j.fuel.2009.03.008>.
- [58] S.D. Stefanidis, K.G. Kalogiannis, E.F. Iliopoulou, A.A. Lappas, P.A. Pilavachi, In-situ upgrading of biomass pyrolysis vapors: Catalyst screening on a fixed bed reactor, *Bioresource Technology*. 102 (2011) 8261–8267. <https://doi.org/10.1016/j.biortech.2011.06.032>.
- [59] M.I. Nokkosmäki, E.T. Kuoppala, E.A. Leppämäki, A.O.I. Krause, Catalytic conversion of biomass pyrolysis vapours with zinc oxide, *Journal of Analytical and*

Applied Pyrolysis. 55 (2000) 119–131. [https://doi.org/10.1016/S0165-2370\(99\)00071-6](https://doi.org/10.1016/S0165-2370(99)00071-6).

- [60] B.B. Uzun, N. Sarioğlu, Rapid and catalytic pyrolysis of corn stalks, Fuel Processing Technology. 90 (2009) 705–716. <https://doi.org/10.1016/j.fuproc.2009.01.012>.
- [61] S.S. Lam, W.A. Wan Mahari, C.K. Cheng, R. Omar, C.T. Chong, H.A. Chase, Recovery of diesel-like fuel from waste palm oil by pyrolysis using a microwave heated bed of activated carbon, Energy. 115 (2016) 791–799. <https://doi.org/10.1016/j.energy.2016.09.076>.
- [62] K. Smets, A. Roukaerts, J. Czech, G. Reggers, S. Schreurs, R. Carleer, J. Yperman, Slow catalytic pyrolysis of rapeseed cake: Product yield and characterization of the pyrolysis liquid, Biomass and Bioenergy. 57 (2013) 180–190. <https://doi.org/10.1016/j.biombioe.2013.07.001>.
- [63] S.-S. Liaw, Z. Wang, P. Ndegwa, C. Frear, S. Ha, C.-Z. Li, M. Garcia-Perez, Effect of pyrolysis temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas Fir wood, Journal of Analytical and Applied Pyrolysis. 93 (2012) 52–62. <https://doi.org/10.1016/j.jaap.2011.09.011>.
- [64] M. Garcia-Perez, X.S. Wang, J. Shen, M.J. Rhodes, F. Tian, W.-J. Lee, H. Wu, C.-Z. Li, Fast Pyrolysis of Oil Mallee Woody Biomass: Effect of Temperature on the Yield and Quality of Pyrolysis Products, Ind. Eng. Chem. Res. 47 (2008) 1846–1854. <https://doi.org/10.1021/ie071497p>.

- [65] J. Akhtar, N. Saidina Amin, A review on operating parameters for optimum liquid oil yield in biomass pyrolysis, *Renewable and Sustainable Energy Reviews*. 16 (2012) 5101–5109. <https://doi.org/10.1016/j.rser.2012.05.033>.
- [66] J. Akhtar, N.A.S. Amin, A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass, *Renewable and Sustainable Energy Reviews*. 15 (2011) 1615–1624. <https://doi.org/10.1016/j.rser.2010.11.054>.
- [67] M. Balat, H. Balat, C. Öz, Progress in bioethanol processing, *Progress in Energy and Combustion Science*. 34 (2008) 551–573. <https://doi.org/10.1016/j.pecs.2007.11.001>.
- [68] G. Vicente, M. Martínez, J. Aracil, Optimisation of integrated biodiesel production. Part I. A study of the biodiesel purity and yield, *Bioresource Technology*. 98 (2007) 1724–1733. <https://doi.org/10.1016/j.biortech.2006.07.024>.
- [69] M. Tabatabaei, M. Aghbashlo, M. Dehghani, H.K.S. Panahi, A. Mollahosseini, M. Hosseini, M.M. Soufiyan, Reactor technologies for biodiesel production and processing: A review, *Progress in Energy and Combustion Science*. 74 (2019) 239–303. <https://doi.org/10.1016/j.pecs.2019.06.001>.
- [70] A. Sharma, S.K. Khare, M.N. Gupta, Three phase partitioning for extraction of oil from soybean, *Bioresour. Technol.* 85 (2002) 327–329. [https://doi.org/10.1016/s0960-8524\(02\)00138-4](https://doi.org/10.1016/s0960-8524(02)00138-4).

- [71] M.H. Mat Yasin, R. Mamat, G. Najafi, O.M. Ali, A.F. Yusop, M.H. Ali, Potentials of palm oil as new feedstock oil for a global alternative fuel: A review, *Renewable and Sustainable Energy Reviews*. 79 (2017) 1034–1049.
<https://doi.org/10.1016/j.rser.2017.05.186>.
- [72] D.E. Starner, A.A. Hamama, H.L. Bhardwaj, *Canola Oil Yield and Quality as Affected by Production Practices in Virginia*, ASHS Press, Virginia, 1999.
- [73] C. Stamigna, D. Chiaretti, E. Chiaretti, P.P. Prosini, Oil and furfural recovery from *Brassica carinata*, *Biomass and Bioenergy*. 39 (2012) 478–483.
<https://doi.org/10.1016/j.biombioe.2011.12.024>.