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Valorisation of Waste Streams within the Agri-Food Sector

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Thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

School of Chemistry and Chemical Engineering, Queen’s University, Belfast

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In Association with Elmgrove Foods Ltd.
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List of Abbreviations

AD – Anaerobic Digestion
AKTS - Advanced Kinetics and Technology Solution
ANIs - Active Nutraceutical Ingredients
APHA – Animal and Plant Health Agency
ATC - Automatic Temperature Compensation
BET - Brunauer-Emmett-Teller
BGE – Background Electrolyte
BREXIT – Great Britain Exiting European Union
BSE - Bovine Spongiform Encephalopathy
BSED - Back-Scattered Electron Detector
CA – Cholic Acid
CAGR- Compound Annual Growth Rate
CDCA - Chenodeoxycholic acid
CE – Capillary Electrophoresis
CHP – Combined Heat and Power
CS – Chondroin Sulfate
Da- Daltons
DAD – Diode Array Detector
DAERA - Department of Agriculture, Environment and Rural Affairs
DAF – Dissolved Air Floatation
DCA - Desoxycholic Acid
DEAE - Diethylaminoethyl
DEFRA – Department of Environment, Food and Rural Affairs
DF – Diafiltration
DMAEMA - Dimethyl Amino Ethyl Methacrylate
DMMB - Dimethylmethylene Blue
DS – Dermatan Sulfate
DSC - Differential Scanning Calorimetry experiments
DTG - Difference Thermo Gravimetry
DVB - Divinylbenzene
ECM – Extra Cellular-matrix
EDMA - Ethylene Glycol Dimethylacrylate
EDS - Energy-Dispersive X-ray Spectroscopy
EFSA - European Food Safety Authority
EHC – Export Health Certificate
EHO - Environmental Health Officer
ELISA - Enzyme-linked Immunosorbent Assay
ELSD - Evaporative Light Scattering Detection
EOF – Electroosmotic Flow
ESI - Electron Spray Ionisation
ETD - Everhart-Thornley Detector
EU – European Union
EULAR- European League Against Rheumatism
FDA – Food and Drug Administration
FOGs – Fats, Oils and Greases
FSA - Food Standards Agency
FTIR - Fourier Transfer Infrared Spectroscopy
FWO - Flynn-Wall-Ozawa
GAG – Glycosaminoglycan
GCA - Glycocholic acid
HA – Hyaluronic Acid
HHP - High Hydrostatic Pressure
HHP-EH - High Hydrostatic Pressure Enzymatic Hydrolysis
HHV – Higher Heating Value
HPLC- High Performance Liquid Chromatography
IBC - Intermediate Bulk Container
ICP-OES Inductively Coupled Plasma with Optical Emission Spectroscopy
IgG - Immunoglobulin G
IP – Intellectual Property
IR – Infrared Spectroscopy
ISO - International Standards Organisation
KAS - Kissinger-Akahira-Sunose
LAMEA - Latin America, Middle East and Africa
LEDCs - Less Economically Developed Countries
MALDI - Matrix Assisted Laser Desorption/Ionisation
MEDCs - More Economically Developed Countries
MF - Microfiltration
MIP – Molecular Imprinted Polymer
MIP – Molecular Imprinted Polymer
MS - mass spectrometry
MWCO – Molecular Weight Cut-Off
NF- Nano-filtration
NI – Northern Ireland
NIR - Near Infrared Reflectance
NMR - Nuclear Magnetic Resonance
OA – Osteoarthritis
OSCS – Over Sulfated Chondroitin Sulfate
PCA – Principle Component Analysis
PCR - Principal Component Regression
PE - Polyethylene
PEG - Polyethylene Glycol
PES - Polyethersulphone
PETRA - Pentraerythritol Tri Acrylate
PLA – Polyacrylamide
PLS - Partial Least Squares method
PP- Polypropylene
PS - Polysulphone
PVA- Polyvinylacetate
RID - Radial Immunodiffusion
RID – Radio Immunodiffusion
RO – Reverse Osmosis
RPM – Revolutions Per Minutes
SEM – Scanning Electron Microscope
SOP – Standard Operating Procedure
SYSADOA - Symptomatic Slow Acting Drug for Osteoarthritis
TCA - Taurocholic acid
TGA - Thermal Gravimetric Analysis
TLC – Thin Layer Chromatography
TMA - Trimethylamine
TRU - Traceable Resource Unit
TSE - Transmissible Spongiform Encephalopathy
UF – Ultrafiltration
UK – United Kingdom
UKECP – UK Export Certification Partnership
USD – United States Dollar
USP – Unique Selling Point
VBC - Vinylbenzylchloride
WFE - Wiped Film Evaporator
XPS – X-ray Photoelectron Spectroscopy
XRD - X-ray Diffraction
XRF - X-Ray Fluorescence
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Many Thanks,
Executive Summary

Over the twenty-year period between 1998 and 2018 the number of full-time farmers within the Northern Ireland (NI) agri-tech sector dropped from 22,524 to 16,964 [1]. As expected, this has also resulted in a commensurate loss in the total cattle livestock which has decreased from 1.77 million to 1.63 million [1]. Despite this, NI beef and sheep meat production accounted for 15% of the total UK output and represents 27% of the gross agricultural turnover in 2017 [1] or £1.3 billion in 2016, while animal by-products accounted for revenues worth £53 million.

While the sector produces a number of high-quality food products, a significant amount of waste is generated during processing. Given increased global competition in the sector and new challenges including climate mitigation it is desired to enhance the overall value and image of the sector and hence valorisation of wastes is increasingly attractive.

This project investigates valorisation of waste streams in the agri-food sector, particularly those which would have been traditionally sent for rendering or exported at low value to other countries for upgrading. The project specifically focuses on the production technologies for specialist chemical compounds from meat by-products and evaluation of the energy potential for plant-based wastes. Overall the data generated within this work aims to boost the agri-tech sector by creating additional revenue streams through diversification of the product portfolio.

The main achievements of this project are associated with the production of traceable nutraceutical products and their intermediaries with proven analysis of the traceability system and the quality of the nutraceuticals exploited. These products will be processed by sustainable separation and extraction techniques that are efficient along with the understanding of global economics and market size of nutraceuticals. Furthermore, focussing upon the release of energy from specific biomass and kinetic modelling of such material in terms of reaction progress, rate of reaction and activation energy associated with each heating rate applied to the material.
4. Berry Pomace

4.1. Introduction

The global demand for food, energy and medicinal products is constantly growing and is expected to continue to grow further to meet the needs of the exponentially increasing population globally [88, 89]. The overdependence on fossil fuels for power generation has led to an alarming decline in oil reserves, directly contributing to global warming[90, 91]. Methods used in order to meet the demands of such a growing population must be done in a sustainable, environmentally friendly and efficient manner. This will ensure that such goods and services are viable for energy production and not detrimental to the natural environment in which we as humans live. As a consequence, the global energy demand alone is expected to grow by approximately 50% over the next 20 years. Projections for the energy demand by 2035 to be 778 EJ. This is putting increased stress on the current fossil fuel energy reserves and impacting climate change throughout the world. With this increase in energy demand, greater focus has been placed on the use of renewable energy sources such as biomass for meeting current and future energy demands in a sustainable manner. This focus of energy production from biomass follows the EU 2020 target, where the energy provided by renewable resources is increased to 20% of the total EU consumption by 2020. A combined target in reduction of EU greenhouse gas emissions to 20%, coupled to an increase in energy efficiency by 20% over a 30-year period (1990-2020) is also stated [92, 93].

The blackcurrant pomace is a mixture of skins, pulp, seeds and stems of the berries[94]. This blackcurrant pomace can be classified within the food waste under the category of biomass materials. The other groupings for biomass energy production are as follows: virgin wood, agricultural residues, energy crops and industrial wastes & co-products [93]. As a food waste, blackcurrant pomace is commonly sent to composting instead of being utilised for sustainable energy production. This is normally carried out post squeezing of the blackcurrants for juice manufacture and chemical treatments for the extraction of anthocyanin and antioxidant products. These anthocyanin and antioxidant products are often used for eyesight therapies, with a reduction in the number of incidents of age-related therapies and the ability to inhibit aggregation of blood platelets alongside the ability of slight relaxation on vascular smooth muscles. Therefore, it has a potential role in reducing factors associated with
chronic inflammatory diseases. More recently, other researchers have focussed on the use of berry pomace for increased fibre and phenol content within foods such as bread and other cereal products, as the pomace can increase the fibre by a reported 15 wt.% in some cases [95, 96].

From the studies of Nawirska and Kwaśniewska, it was reported that the pomace was used for dietary fibre purposes and was characterised by a dietary fibre content of 90.8 wt.%. The percentage mass of hemicellulose, cellulose and lignin are contents of 25.3, 12.0 and 59.3 wt.%, respectively whilst pectin accounts for only 2.73 wt.%. Overall, the lignin and hemicellulose content accounts for 84 wt.% of the dietary fibre in the pomace [95]. Furthermore, there may be the opportunity to develop the biochar material from the pyrolysis process into a potentially useful adsorbent material for heavy metal extraction from contaminated water containing lead and cadmium [97, 98]. This novel approach for biochar production from biomass sources has found use before in this area of wastewater treatment. It has been reported previously, that the biomass material once pyrolysed into biochar has had its structural and surface properties greatly modified, due to the submissively high pyrolytic temperatures [93]. One example of this application is the use of miscanthus biochar to remove cadmium from aqueous solutions. From these previous findings, this biomass material possesses the desirable properties of a porous structure, rich mineral components in the char and least of all; a large surface area [93].

At present, there are 12 varieties of blackcurrant grown within the UK, with major drinks company Ribena harvesting and processing most of the crop, estimated to be worth £10million. As with all fruit and wood crops, the blackcurrants require a period of chilling before starting the growth stage in early spring. Due to the various varieties of blackcurrants, different growing conditions are required. Approximately 35% of the current UK grown, require 1800 hrs of chilling below 7 °C, whilst other variants require lower temperatures and others tolerating higher temperatures if the chilling period lasts longer [99]. These growing conditions are best suited in Baltic countries such as Russia, Ukraine, Poland and Hungary. With the global production of the blackcurrants reaching 655,000 metric tonnes per year in 2016, Russia and Poland accounted for 60.3 and 25.4%, respectively, of the production volume [100]. Therefore, there are large expanses of this biomass material available in many demographic regions. An estimated two-thirds of the market is held for the concentrated drinks sector. Blackcurrant pomace-post-treatment for extraction of
anthocyanins and antioxidants is generally sent to anaerobic digestion and fermentation in most processing facilities for biochemical conversion. However, little research is currently available on the calorific value and the kinetic modelling of this material as an energy crop for thermochemical conversion. Thermochemical conversion takes one of four forms of technologies available such as combustion, pyrolysis, gasification and liquefaction [93]. Focussing on combusting the biomass, initially for heat and electrical energy will result in the production of solid waste material, ash. This substance may have a high composition of Nitrogen-Phosphorous-Potassium (N-P-K), similar to most fertilisers and so may have potential to be used in the agricultural sector [101]. If this ash can be used as an organic fertiliser, this will complete the full cycle of this material in a sustainable manner and thus, directly support and facilitate the idea of the circular economy.

For a better understanding of the prediction of the real-life dynamics, mechanism and behaviour of the biomass feedstock as it undergoes combustion for energy production, the thermal and kinetic analysis is required. Herein a focus on physicochemical study, thermal investigation and kinetic modelling approach for lignocellulosic biomass material in the form of blackcurrant pomace will be investigated. This is a waste product from the food and drinks sector yet to be utilised or reported on for energy production. The model-free (iso-conversional) kinetic modelling approach has an advantage over the model fitting methods in determining the kinetic data of lignocellulosic biomass thermal decomposition. One such reason is the reaction mechanism is not required and also the kinetic parameters such as activation energy and pre-exponential constant are evaluated at different extents of conversion and not considered constant. Investigating the thermal kinetics with this method will enable the approximation of the activation energy ($E_a$) requirement as a function of the extent of conversion with no pre-requisite requirement of the decomposition reaction mechanism. This can be obtained through a varied range of thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments under different heating rates using the Advanced Kinetics and Technology Solution (AKTS) software [102].

Due to all biomass being composed of three constituent parts: cellulose, hemicellulose and lignocellulose, it is inaccurate to state that the biomass possesses only one $E_a$ and therefore, as a result fits the model-free methods: Kissinger, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS). In effect, biomass can possess up to
nine separate $E_a$ values, due to a potential nine-step mechanism as the cellulose, hemicellulose and lignocellulose may each contain three $E_a$. As previously studied by Mong et al. for the kinetic study of horse manure, the FWO and KAS methods were applied and found to produce an $E_a$ of 148.47 kJ.mol$^{-1}$ [102]. Similarly, Otero et al. produced an $E_a$ of 212 kJ.mol$^{-1}$ via the FWO method for cattle manure [103]. This is contrary to that reported by Osman et al. where the activation energies for miscanthus varied from 40–165 kJ.mol$^{-1}$ via the differential iso-conversional method throughout the progress of the reaction [93]. This changing of $E_a$ is due to the dehydration of water from the material at the start of the reaction mechanism, followed by the breakdown down of the cellulose content before a slight drop in $E_a$ for the hemicellulose content, before increasing for the lignocellulose content.

From the literature, there is limited knowledge available on the $E_a$ of blackberry pomace to help perform the kinetic modelling. The only values available for the $E_a$ focus on blackberry seed oil. It was reported by D. M. Micić et al. that the $E_a$ for blackberry seed oil was 101 ± 4 and 90 ± 10 kJ.mol$^{-1}$ for the onset temperature ($T_{on}$) and the first peak ($T_{p1}$), respectively. $T_{on}$ and $T_{p1}$ correspond to the DSC curve for the blackberry seed oil [104]. Despite these values relating to the seed oil, these may be comparative and useful as the pomace material which this study is focused on contains seeds, stems and the pulp. Kayran et al. reported their studies on the energy content within apricot pomace and its uses in industry. The $E_a$ for this biomass crop waste material was found to be 19.41 kJ.mol$^{-1}$, thereby complying to the activation energy limits of other food materials, 12.7 - 110 kJ.mol$^{-1}$ [105, 106]. In comparison to other biomass from different agricultural by-products such as carrot pomace, apple pomace, industrial grape pomace and apricot kernels, their activation energies were 23.05, 24.51, 19.27 and 16.5 kJ.mol$^{-1}$, respectively [105, 107-109]. In addition, further studies have been conducted on the thermal decomposition of olive pomace under torrefaction operating conditions and the iso-conversional kinetic analysis of such material. From the work conducted by Brachi et al., the $E_a$ of olive pomace varies from 167.94 - 994.09 kJ.mol$^{-1}$ (linear) and 162.59 - 1069.74 kJ.mol$^{-1}$ (non-linear), with the trend being set by the degree of conversion from 0.05 to 0.95 [110].

According to the authors’ knowledge, there is no pre-existing detailed work that has been performed on the kinetic modelling of blackberry pomace thermal processes, along with its use for energy production.
4.2. Experimental

4.2.1. Materials

The blackberry pomace used in this study was obtained from industrial partners, with the material originally being harvested in the southern hemisphere in the harvesting season of 2018. The pomace material was initially passed through a solvent and press extraction process to remove the anthocyanins and antioxidants for pharmaceutical and nutraceutical use. This spent material is then removed from the process and dumped into a waste skip on site before being transported (with an associated cost), to a local composting company. The sample obtained is completely non-homogeneous from the skipped material and was dried in an oven prior to postal of the packaged material.

4.2.2. Pomace Biomass Characterisation

Powder X-ray diffraction (XRD) was carried out using a PANalytical X’Pert Pro X-ray diffractometer. This diffractometer was equipped with a CuKα X-ray source with a wavelength of 1.5405 Å. The diffractograms were collected up to 2θ = 80°. The X-ray tube was set at 40 kV and 40 mA. Fourier Transform Infrared (FT-IR) spectroscopy was operated using a Perkin Elmer Spectrum, a beam splitter in the wavenumber range of 4000 – 400 cm⁻¹. XPS was performed using JEOL (JEM-2100F) with a quartz monochromator Al Kα radiation of energy 1486.6 eV. For construction and fitting of synthetic peaks of high-resolution spectra, mixed Gaussian-Lorentzian functions with a Shirley-type background subtraction were used. Raman spectroscopy (XploRA from Horiba) was used to probe on the powder surface of samples (P1 and P2) with continuous 532 nm laser excitation. The Raman spectra were collected from 100-2500 cm⁻¹ using a TE-cooled CCD camera (Syncret) attached to the monochromator of a spectrometer with 600 gr.mm⁻¹. The spectra were obtained by collecting 20 acquisitions. Brunauer-Emmett-Teller (BET) analysis was performed using a Micromeritics ASAP 2020 system. BET surface area and pore volume were measured by N₂ adsorption and desorption isotherms at liquid nitrogen temperature (-196 °C).

Compositions of the pomace biomass waste were characterised by means of proximate and ultimate analyses. Elemental (C, H and N) Analysis was performed using a Perkin Elmer PE2400 CHNS/O Elemental Analyser. The oxygen content was calculated by difference from the data obtained by a Perkin Elmer PE2400 CHNS/O Elemental Analyser. Proximate analysis was carried out according to the ASTM method to
determine the % of moisture (ASTM D2867-95), volatile matter (ASTM D5832-95), ash content (ASTM D2866-94), char and fixed carbon (by difference) [111, 112]. Bomb calorimetry was conducted using a Parr 6200 oxygen bomb calorimeter. Char and volatile contents were determined using Thermogravimetry (TGA), with heating to 900 °C at a rate of 10 °C.min⁻¹ and holding the temperature for 10 min to ensure constant final weight [113]. Again with the TGA, % Ash was obtained by heating to 500 °C with a heating rate of 10 °C.min⁻¹ then heating to 575 °C with 2.5 °C.min⁻¹ and holding for 10 min [113]. SEM was carried out on a FEI Quanta 250 FEG MKII with a high-resolution environmental microscope (ESEM) using XT Microscope Control software and linked to an EDX detector. Two types of detectors were used in SEM analysis; the Everhart-Thornley Detector (ETD) which is used to detect secondary electrons emitted from the sample and BSED which is used to measure the backscattered electrons from the sample, where the elements of higher atomic number appear brighter in the image due to emitting a large number of back-scattered electrons (BSE). The EDX used was a 10 mm² SDD Detector-x-act from Oxford Instruments which utilizes Aztec® EDS analysis software. Both systems used the same chamber. TGA was performed at a specific heat range with different heating rates of 2, 4, 6, 8 and 10 °C min⁻¹, in a stream of dry air flowing at 40 cm³.min⁻¹, using a simultaneous thermal analysis Mettler Toledo (TGA/DSC) Thermogravimetric analyser Pyris TGA/DSC1. Changes in mass of the sample were recorded during the ramping operation. DSC was used to determine the heat liberated in W.g⁻¹. For the kinetic modeling, the weights of the samples were between 7.22 and 7.74 mg to reduce the effect of heat and mass transfer on the data obtained from the DSC machine. Kinetic modeling was run using AKTS (Advanced Kinetics and Technology Solutions) software.
4.3. Results and Discussion

4.3.1. Characterisation results

Figure 65 shows the XRD and FTIR results of both pomace biomass and biochar. The XRD diffractogram of both pomace samples (Figure 65 (a)) displays two different phases; amorphous and crystalline cellulose. The latter cellulose appeared with diffraction lines at $2\theta = 22^\circ$, corresponding to the crystallographic plane (002) with JCPDS data 03-0289 while the amorphous cellulose at $2\theta = 18^\circ$. The crystallinity index ($%\text{CRI}$) which was calculated according to equation 8, gives the measure of crystalline cellulose for amorphous regions.

$$%\text{CRI} = \frac{(I_{002} - I_{\text{am}})}{I_{002}} \times 100$$

Equation 8. Crystallinity Index Equation

Where: $I_{\text{am}}$: is the low-intensity peak of the amorphous region at $2\theta = 18^\circ$

$I_{002}$: is the highest peak (002) intensity of the crystalline fraction at $2\theta = 22^\circ$

The $%\text{CRI}$ calculated accordingly was 37.5 % which confirms the presence of the larger fraction of amorphous cellulose, unlike the miscanthus which showed 77.1% and 74% [91, 114]. However, this result is in line with other work done on fruit pomace which showed 33.7% CRI [115]. Even with the pomace biochar, $%\text{CRI}$ decreased to 35.8% compared to the pomace biomass as shown in Figure 65. The FTIR spectra of the pomace biomass and its biochar are shown in Figure 65 (b). The pomace biomass showed absorption bands at approximately 3433, 2933, 2860, 1740, 1649, 1455 and 1142 cm$^{-1}$, which correspond to O-H stretching, C-H symmetrical and asymmetric vibration mode of methyl and methylene groups stretching, CH$_2$ stretching vibration, C=O (conjugated), C=O (non-conjugated or O-H), C=O bending and C-O-C stretching, respectively [116, 117]. The aforementioned absorption bands are indicative of the cellulose fingerprint region. The band at 2945 and small band at 3000 cm$^{-1}$ are both indicative of cellulose as well as the band at 1455 cm$^{-1}$ due to the C-H stretching. The ester stretching band of C-O-C (1142 cm$^{-1}$) also supports the presence of cellulose within the pomace biomass structure. On the other hand, by calcining the pomace biomass which led to the destruction of functional groups within the structure of the lignocellulosic biomass as shown in the FTIR spectra of pomace biochar. The absorption band at 1599 cm$^{-1}$ is attributed to the C=C symmetrical stretching in the carbonaceous composition of the char [118].
Figure 65: Shows the XRD patterns of pomace biomass and biochar (a) along with the FTIR results of both samples (b).

Figure 66 (a-c) shows the SEM images of the pomace biomass which showed a bulky material with a non-porous structure. This is in line with the S_{BET} results that showed a very low surface area along with pore volume of 0.42 m$^2$.g$^{-1}$ and 0.000005 cm$^3$.g$^{-1}$, respectively as seen in Table 21. On the other hand, pomace biochar (Figure 66 (d-e)) showed a porous structure, where the pyrolysis opened up new pores in the carbonaceous structure of the char. Again, the results are in agreement with the S_{BET} results that showed a significant increase in the surface morphology in the char with
surface area and pore volume of 44.7 m$^2$.g$^{-1}$ and 0.019 cm$^3$.g$^{-1}$, respectively. It is worth noting that the pomace ash showed a surface area and pore volume of 6.9 m$^2$.g$^{-1}$ and 0.008 cm$^3$.g$^{-1}$, respectively. The SEM images of the pomace ash are shown in Figure S1 (supplementary information) using BSED where heavier elements appear brighter. The EDX data of pomace biomass, biochar and ash are shown in Figure S2 (a-c), where the surface structure of the pomace biomass showed only carbon and oxygen with 71.6 and 28.4 wt.%, respectively. While the pomace biochar showed minor contribution of inorganic elements such as K, P, Mg with wt.% composition of 2.3, 1.1 and 0.2 wt.%, respectively. Interestingly, those inorganic elements significantly increased in the pomace ash with values of 28.5, 17.3, 2.5 wt.%, respectively along with other elements such as Ca, Na and S with wt.% of 8.0, 1.5 and 1.2 wt.%, respectively. The proximate/ultimate analysis in Table 21, showed that pomace biomass is a good candidate to be used as an energy crop due to its high higher heating value (HHV) of 21.36 MJ.kg$^{-1}$ compared with other biomass energy crops such as miscanthus with a calorific value of (16.58 MJ.kg$^{-1}$) [91]. Osman recently reported that the potato peel waste showed HHV of 15.73 MJ.kg$^{-1}$ [119]. Furthermore, the results showed that the pomace ash left after combustion could be used in the fertiliser industry due to the high K and P in its compositions as the typical fertiliser is N-K-P.
Figure 66: Shows the SEM images of pomace biomass (a-c) and biochar (d-f) at different levels of magnification using ETD detector.
Raman spectroscopy was utilised to detect the structural defects and disorder in the pomace biomass and its biochar as shown in Figure 67 (a). It showed the different carbon allotropes in both samples with two distinct spectra at 1341 and 1580 cm\(^{-1}\), which attributed to D and G bands, respectively. Crystalline graphite G corresponds to the in-plane vibrations of the sp\(^2\) chain with E\(_{2G}\) symmetry or to doubly degenerate deformation vibrations of the hexagonal ring [120]. While the D band “disorder” in graphite materials contain defects with A\(_{1g}\) symmetry and limited crystallite size. The I\(_D/I_G\) ratio was calculated according to the D and G bands intensities and was 0.924, indicating a low degree of crystalline graphitic structure which is in line with the XRD results in Figure 65. The structure of the pomace biomass significantly affected by the pyrolysis where the two bands dramatically decreased in intensity with the pyrolysis temperature as shown in Figure 67 (a). The surface species of the pomace biomass and biochar were detected using the XPS technique as shown in Figure 67 (b, c for pomace biomass and d, e for biochar). The C1s peak for both of them (Figure 67 (b, d) was mainly at the binding energy of 284.4 eV, which is attributed to C-C and C-H bonding. Furthermore, pomace biomass showed a small peak at around 287.2 eV, which is attributed to the C=O in the carbonyl group in the biomass structure, while pomace biochar showed a minor contribution of N-C=O in char structure [121]. The oxygen surface species were significantly changed with the pyrolysis as pomace biomass showed mainly oxide (O\(^2-\) at 530.1 eV) and carbonyl oxygen (C=O at 528.5 eV), while pomace biochar showed hydroxide (at 531.1 eV) and a higher binding energy carbonyl (at 533.4 eV) along with minor contribution of gas-phase CO\(_2\) at 536.4 eV. The results implying that the oxide species decreased during the formation of carbonaceous char and shifted to higher binding energy of C=O bonding in biochar structure as seen in Figure 67 (e) [122]. The results are in line with the EDX results that showed higher alkaline metals present in the biochar structure that might increase the basicity of the structure, hence absorbed CO\(_2\) on the surface. Figure S3 shows the XPS surveys of pomace biomass and biochar where the obvious difference was the presence of potassium (K 2p) peak in the biochar spectra.
Figure 67: Shows a) Raman Spectroscopy of both pomace biomass and biochar along with the XPS Spectra of C1s O1s for pomace Biomass (b, c) and pomace biochar (d, e).
Table 21. Physicochemical characterisations of pomace biomass waste.

<table>
<thead>
<tr>
<th>samples</th>
<th>% C</th>
<th>48.06</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental composition</td>
<td>% H</td>
<td>6.13</td>
</tr>
<tr>
<td>(wt% on a dry basis)</td>
<td>% N</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>% S</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>% O</td>
<td>43.11</td>
</tr>
<tr>
<td>Proximate analysis</td>
<td>Moisture</td>
<td>8.33</td>
</tr>
<tr>
<td>(wt% on a dry basis)</td>
<td>Volatile</td>
<td>72.8</td>
</tr>
<tr>
<td></td>
<td>Char</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td>Fixed carbon</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td>Ash</td>
<td>3.73</td>
</tr>
<tr>
<td></td>
<td>HHV&lt;sup&gt;a&lt;/sup&gt;</td>
<td>21.36</td>
</tr>
<tr>
<td></td>
<td>LHV&lt;sup&gt;b&lt;/sup&gt;</td>
<td>19.57</td>
</tr>
<tr>
<td>EDX analysis</td>
<td>C</td>
<td>71.6</td>
</tr>
<tr>
<td>(wt% on a dry basis)</td>
<td>O</td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>--</td>
</tr>
<tr>
<td>S&lt;sub&gt;BET&lt;/sub&gt; results</td>
<td>SBET&lt;sup&gt;m2.g&lt;sup&gt;-1&lt;/sup&gt;&lt;/sup&gt;</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>Pore volume&lt;sup&gt;(cm&lt;sup&gt;3&lt;/sup&gt;.g&lt;sup&gt;-1&lt;/sup&gt;)&lt;/sup&gt;</td>
<td>0.000005</td>
</tr>
<tr>
<td></td>
<td>Pore size&lt;sup&gt;(Å)&lt;/sup&gt;</td>
<td>18.9</td>
</tr>
</tbody>
</table>

<sup>a</sup> High heating value (kJ. g<sup>-1</sup> dry feedstock) in MJ.kg<sup>-1</sup>

<sup>b</sup> Low heating value (kJ. g<sup>-1</sup> dry feedstock) in MJ.kg<sup>-1</sup>

4.3.2. Kinetic modelling of pomace combustion

Combustion is best described as thermochemical conversion based on heating material in a temperature range with an abundance of oxygen or oxygen-rich environment. In this particular case, biomass, in the presence of air in a temperature range of 800-1000°C. Subsequently, from combusting biomass, this results in the conversion of chemically stored energy in the material to heat and kinetic energy. This energy can be further transformed into electrical energy via means of a CHP unit in the form of a
biomass boiler. As a result, by-products from the combustion process are ash and hot gases. While pyrolysis is occurring in an inert atmosphere usually in the form of an inert purging gas. Gasification is the process in which exposure of a material (biomass) to exceedingly high temperatures of 800-1500 °C in rich oxygen environment until the temperature is self-sustaining and the oxygen content is then restricted or cut off. The material is converted into a gaseous combustible mixture which generally possesses a low energy content. This can be directly burnt or subsequently used as a fuel for gas turbines and gen-sets. Thus, studying the thermal and kinetic modelling study of this material will serve as guidance as to how the pomace could act as a potential fuel source and its behaviour with the thermochemical conversion. Furthermore, identifying the crucial factors and parameters in the thermochemical conversion and ultimately which method is best suited for this biomass waste.

4.3.3. Differential Iso-conversional kinetic model

4.3.3.1. AKTS – DSC (Differential Scanning Calorimetry)

The activation energy and the kinetic parameters of pomace biomass combustion were calculated from the DSC curves with different heating rates (2, 4, 6 and 8 °C.min\(^{-1}\)) under air atmosphere. To ensure the reproducibility of the DSC data, the heating rate of 4 °C.min\(^{-1}\) was repeated. To have a better understanding of the combustion process of pomace biomass, AKTS software was employed to calculate the activation energy (\(E_a\)) and the pre-exponential factor herein. Different iso-conversional methods were utilised such as ASTM-E698, Ozawa-Flynn-Wall and differential iso-conversional method such as the Friedman method. It is well known that the model-free (iso-conversional) method is preferable than that of the model fitting method due to various reasons. Firstly, the kinetic data may fit more than one model at the same time along with the error related to the model fitting method. Secondly, this method allows determination of activation energy and pre-exponential constant at different extents of conversion and its subsequent changes and finally, no prior knowledge of the reaction mechanism is required. Thus, herein, the iso-conversional method was used to detect the kinetic parameters using different heating rates (from 2-8 °C.min\(^{-1}\)) as a function of reaction conversion (\(\alpha\)).

Previous literature studies showed the mechanism of lignocellulosic biomass combustion is a complicated process that can potentially happen in nine possible
parallel reactions at the same time. Pyrolysis, on the other hand, deals with biomass material being converted into products in the three states of matter: solid, liquid and gas [123]. Pyrolysis is the initial physical-chemical processing step which occurs in all thermo-chemical reaction sequences for gasification or combustion. In addition, from biomass, stable liquid hydrocarbons can be produced by the process of liquefaction. This liquefaction process involves the use of low temperatures and high hydrogen pressures, 200-400 °C and 2-20 x 10^6 Pa, respectively [93]. Ten-step mechanism of pyrolysis is proposed according to the parallel decomposition reactions of cellulose, hemicellulose and lignin as below:

1) Cellulose decomposition
   a) Cellulose → Char + H₂O + Active Cellulose
   b) Active Cellulose → Char + H₂O + Primary Vapours + Secondary Gas
   c) Primary Vapours → Secondary Gas + Secondary Tar

2) Hemicellulose decomposition
   a) Hemicellulose → Volatile Fraction + Intermediate Hemicellulose
   b) Intermediate Hemicellulose → Char + Volatile Gases
   c) Primary Volatiles → Secondary Gas + Secondary Tar

3) Lignin decomposition
   a) Lignin → Char + Volatile Gases
   b) Lignin → Tar
   c) Lignin → Gas + Reactive Vapours
   d) Primary Volatile Vapours → Secondary Gas + Secondary Tar

In this proposed mechanism, the three different components of biomass (cellulose, hemicellulose and lignin) behave differently and independently to each other with the cellulose separating into active cellulose during the reaction. Despite these components behaving independently, each component pyrolyses to produce char (steps 1a, 1b, 2b and 3a) [124]. The degree and classification of the char throughout the mechanism are unknown, unlike the nine-step mechanism as reported by Osman et al. [93]. Primary gas is produced in steps 3a and 3c by pyrolysis of lignin, while primary tar is produced by lignin in step 3b. As the reaction progresses for each of these components, secondary products are produced such as secondary gas (1b, 2c and 3d) and secondary tar (1c, 2c and 3d) by pyrolysis of the active cellulose and primary.
vapours, respectively. The volatile fraction gases are further processed to produced chemicals such as acetone, methanol and recycled back to the pyrolysis reactor to provide heat, while the tar/bio-oil fractions are refined to levoglucosan, acetic acid and automotive fuel[124]. Thus, a single $E_a$ value in either combustion or pyrolysis processes cannot describe the kinetic parameters accurately [93, 125]. Consequently, the iso-conversional method is considered the best method in this case of biomass combustion/pyrolysis.

The rate of the thermal decomposition of the pomace biomass can be defined as a function of reaction conversion progress ($\alpha$) and temperature according to the iso-conversional method. Where $\alpha$ is calculated from the initial, actual and final mass of lignocellulosic biomass. Arrhenius equation which is shown in Table 2 described the temperature-dependent function of the kinetic parameters i.e. $E_a$ and pre-exponential factor ($k_0$). Thus, as a combination of the rate and Arrhenius equations, the thermal decomposition of pomace biomass can be described as in Equation 9 below:

$$\frac{d\alpha}{dt} = k_0 e^{(-\frac{E_a}{RT})} f(\alpha)$$

Equation 9. Isothermal conversion, combining rate and Arrhenius equations.

Usually, the iso-conversional method (non-isothermal) uses different linear heating rates, $\beta = \frac{dT}{dt}$, and so the thermal process of pomace biomass can be described as in Equation 10 below:

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} e^{(-\frac{E_a}{RT})} f(\alpha)$$


The non-isothermal iso-conversional methods such as ASTM-E698, Flynn-Wall and Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods are shown in Table 2. While the Friedman method represents the isothermal iso-conversional method in Table 2.
Table 22. Shows the non-isothermal and iso-thermal iso-conversional methods used in kinetic modelling.

<table>
<thead>
<tr>
<th>Methods types</th>
<th>Method Name</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Isothermal</td>
<td>Arrhenius Equation</td>
<td>( k = k_0 \frac{-E_a}{RT} )</td>
</tr>
<tr>
<td></td>
<td>ASTM-E698</td>
<td>( \frac{\beta}{d\alpha} \frac{da}{dt} = k_0 e^{\left(\frac{-E_a}{RT}\right)} (1 - \alpha) )</td>
</tr>
<tr>
<td></td>
<td>Flynn-Wall and Ozawa (FWO)</td>
<td>( \ln \beta = \ln \left( \frac{k_0 \cdot E_a}{R \cdot g(\alpha)} \right) - 5.331 - 1.052 \frac{E_a}{RT} )</td>
</tr>
<tr>
<td></td>
<td>Kissinger-Akahira-Sunose (KAS)</td>
<td>( \frac{ln \beta}{T^2} = \ln \left[ \frac{k_0 \cdot R \cdot g(\alpha)}{E_a \cdot g(\alpha)} \left(1 - \frac{2RT}{E_a} \right) \right] - \left( \frac{E_a}{RT} \right) )</td>
</tr>
<tr>
<td>Isothermal</td>
<td>Friedman (Iso-conversional)</td>
<td>( \ln \beta \frac{d\alpha}{dT} = \ln \left[ k_0 f(\alpha) \right] - \frac{E_a}{RT} )</td>
</tr>
</tbody>
</table>

Figures 68 and 69 show the heat flow of the pomace biomass combustion with different heating rates of 2 and 4 °C.min\(^{-1}\) (Figure 68) and 6 and 8 °C.min\(^{-1}\) (Figure 69) where the coloured and black curves are for practical and theoretical data from simulation, respectively. It is not surprising that there was a significant shift in the ignition temperature by 49 °C between the lowest and the highest heating rates. The burnout temperature showed an even higher shift by 88 °C, as shown in Figure S4. The decomposition temperature at low heating rate i.e. 2 °C.min\(^{-1}\) was in the temperature range of 194.8-557 °C, while at high heating rate (8 °C.min\(^{-1}\)) was in the range of 244-645 °C. Figures 68 and 69 show that the peak height was shifted from 0.5 to 5.5 W.g\(^{-1}\) by increasing the heating rates from 2 to 8 °C.min\(^{-1}\).
Figure 68: Heat flow of the pomace biomass combustion with heating rates 2 °C.min⁻¹ (top) and 4 °C.min⁻¹ (bottom) under air atmosphere. The curve signals are blue, the integration under the curve is yellow and simulation is black.
Figure 69: Heat flow of the pomace biomass combustion with heating rates 6 °C.min⁻¹ (top) and 8 °C.min⁻¹ (bottom) under air atmosphere. The curve signals are blue, the integration under the curve is yellow and simulation is black.
The reaction conversion progress ($\alpha$) versus temperature for the pomace combustion is shown in Figure 70 with coloured curves for the practical results, while black-dashed curves for the theoretical calculations by AKTS software. Overall, there was a distinct match between the practical and theoretical calculations with $R^2=0.9907$. All of the experimental results fit the same shape for reaction progress, with the highest heating rate ($8 \, ^\circ\text{C.min}^{-1}$) being the furthest right curve and the lowest heating rate ($6 \, ^\circ\text{C.min}^{-1}$) being the furthest left curve, respectively.

![Figure 70: Reaction progress ($\alpha$) versus the temperature for the pomace biomass combustion where the coloured and dashed black curves show the practical and theoretical calculations, respectively.](image)

Figure 71 shows the reaction rate versus the temperature for the pomace biomass combustion where the coloured and dashed black curves show the practical and theoretical calculations, respectively. Again, there is a perfect match at lower heating rate i.e $2-6 \, ^\circ\text{C.min}^{-1}$, while at $8 \, ^\circ\text{C.min}^{-1}$, there was slight deviation which may be due to the large amount of heat generated from the combustion process at $8 \, ^\circ\text{C.min}^{-1}$. This result is in line with other work that showed the same trend at high heating rate [93]. Furthermore, the theoretical and practical results both showed a clear shift toward
higher temperature with increasing the heating rate from 2 to 8 °C min\(^{-1}\). The first decomposition peak appeared at 303, 323, 330 and 341 °C at heating rates of 2, 4, 6 and 8 °C min\(^{-1}\), respectively. While the second decomposition peak was present at 463, 502, 518 and 533 °C at heating rates of 2, 4, 6 and 8 °C min\(^{-1}\), respectively. The maximum reaction rate for all the heating rates tested occurred at the second decomposition peak. Subsequently, the maximum reaction rates were found to be 0.000164, 0.000301, 0.000427 and 0.000578 s\(^{-1}\) for 2, 4, 6 and 8 °C min\(^{-1}\), respectively. The reaction rate increased six times by increasing the heating rate from 2 to 8 °C min\(^{-1}\) as seen in Figure 71. The results are in agreement with the work done by Kumar et al. [126].

![Figure 71: Reaction rate versus the temperature for the pomace biomass combustion where the coloured and dashed black curves show the practical and theoretical calculations, respectively.](image)

\[ R^2 = 0.99544 \]
4.3.3.2. Kinetic modelling discussion of pomace combustion (DSC)

In general, lignocellulosic biomass shows three decomposition stages during the thermal decomposition. Similar biomass to the blackcurrant pomace used herein such as olive pomace showed three distinct thermal decomposition zones. The first zone was the drying and evaporation of water up to 150 °C. This is closely followed by phase two, the devolatilisation of hemicellulose and cellulose at 150-400 °C, while lignin was decomposed in phase three at 400-800 °C [127]. Similarly, the thermal degradation behaviour of grape pomace in an inert atmosphere exhibited at temperatures below 130 °C, there was a slight loss of weight due to evaporation of moisture and volatilisation of small organic molecules. Decomposition of hemicellulose occurred around 200 °C and reached the maximum weight loss rate at 273 °C [128]. The hemicellulose decomposition overlapped with cellulose decomposition as like the olive pomace however, the greatest cellulose breakdown occurred at 300 to 320 °C. Lignin was the final component to decompose at approximately 100 °C in excess of the cellulose at 420 °C. The main degradation occurs at temperatures between 200 and 483 °C [128]. Thus, due to the complexity of pomace thermal decomposition, it is not feasible to represent the kinetic parameters with the model-fitting approach nor a single activation energy value for that complicated process.

The reaction mechanism for miscanthus thermal decomposition was proposed to be 3, 5 or 9 reaction-step mechanism [93]. The ASTM-E698 method was used to calculate the apparent activation energy (E<sub>a</sub>=88.6 kJ mol<sup>-1</sup>) based on Equation in Table 22 and as shown in Figure 72. The ASTM-E698 was used to calculate the kinetic parameters of olive pomace thermal decomposition where the E<sub>a</sub> was 170.99 kJ.mol<sup>-1</sup> and pre-exponential factor was 6.46 x10<sup>12</sup> s<sup>-1</sup> [129]. ASTM I method was used to calculate the E<sub>a</sub> of different biomass feedstocks such as miscanthus, poplar wood and rice husk which showed values of 143, 138, 159 kJ.mol<sup>-1</sup>, respectively. While, ASTM II methods showed 141, 132 and 149 kJ.mol<sup>-1</sup>, respectively [130]. D. M. Micić et al. reported E<sub>a</sub> values for blackberry seed oil was 101 ± 4 and 90 ± 10 kJ.mol<sup>-1</sup> for the onset temperature (T<sub>on</sub>) and the first peak (T<sub>P1</sub>), respectively. T<sub>on</sub> and T<sub>P1</sub> correspond to the DSC curve for the blackberry seed oil [104].

Again, due to the complexity of the lignocellulosic biomass decomposition, one single E<sub>a</sub> value is inadequate to define the thermal decomposition, thus the ASTM-E698
method is imprecise herein. Hence, the iso-conversional method is used herein to calculate the kinetic parameters ($E_a$ and $K_0$) as a function of $\alpha$ [131].

![Graph](image)

**Figure 72:** Kinetic parameters calculated for pomace combustion by different methods (a) $E_a$ using the ASTM-E698 method and (b) $E_a$ and pre-exponential factor using the Flynn-Wall and Ozawa (FWO) method.

Figure 72 (b) shows the kinetic parameters calculated using FWO, which is more accurate than that of ASTM-E698 method as the $E_a$ and $K_0$ are both changing during the reaction progress. The $E_a$ showed values in the range of 50-140 kJ mol$^{-1}$ during the reaction progress. Horse and cattle manure which have been previously studied to show that horse manure combustion has activation energies within the ranges of 176.2-293.6 kJmol$^{-1}$, 175.6-300.1 kJmol$^{-1}$ and 170.2-244.1 kJmol$^{-1}$ for the methods of FWO, KAS and Friedman, respectively. Whilst dried cattle manure has a larger $E_a$ range from 119-348 kJmol$^{-1}$, however, in comparison, the $E_a$ from the dried material is close to the range of activation energy from fresh cattle manure with the respect that
both cattle and horses are grass-grazing herbivores [103]. Moreover, with the aid of AKTS software, the kinetic parameters were calculated with the differential iso-conversional method as shown in Figure 73 (a, b). The natural logarithm of the reaction rate in (s⁻¹) versus the inverse temperature is shown in Figure 73 (a), while the calculated $E_a$ and $K_0$ are shown in Figure 73 (b). At the beginning of the thermal decomposition where $\alpha = 0$, the $E_a$ was 84.3 kJ mol⁻¹ then quickly declined to 76.8 kJ mol⁻¹ as the $\alpha$ was 0.01. The $E_a$ value then gradually increased to 108.4 kJ mol⁻¹ as $\alpha$ reached 0.05, followed by a gradual decrease to 92 kJ.mol⁻¹ when $\alpha$ was 0.2. Then the $E_a$ values showed a variation during the reaction with values of 113, 95 and 188 kJ.mol⁻¹ as the reaction proceeded with $\alpha$ values of 0.4, 0.7 and 1, respectively. Hence, the differential iso-conversional method showed the most realistic values for the kinetic parameters than other methods, along with demonstrating the presence of numerous reactions during the pomace biomass thermal decomposition.
Figure 73: Combustion kinetic parameters calculated with the differential iso-conversional method, a) natural logarithm of the reaction rate in (s\(^{-1}\)) versus the inverse temperature, b) \(E_a\) and \(\ln k_0\).

4.3.3.3. The isothermal prediction of pomace combustion

The kinetic prediction of isothermal combustion of pomace biomass produced using AKTS software is shown in Figure 74 (a). It is evident that temperature higher than 500 °C is required in order to complete the reaction within 60 minutes reaction time. At a temperature of 400 °C for a reaction time of 60 minutes, the reaction progress was only 68% (\(\alpha=0.68\)), while at 460°C, the reaction progress had increased to 91% within the same reaction time. At temperatures of 560 °C and 600°C, the reaction had achieved 100% completion (\(\alpha=1\)) after 30 and 6 minutes respectively. This simulation profile of isothermal combustion of berry pomace is comparative with other lignocellulosic material as reported in the miscanthus study [93]. The reported heat released in the case of the miscantus isothermal process was 6484.7 J.g\(^{-1}\), while herein, it was 8283.7 J.g\(^{-1}\), implying that blackcurrant pomace waste is a promising energy crop compared to other biomass energy crops. This is not surprising when considering the calorific value of the berry pomace is marginally higher (21.36 MJ.kg\(^{-1}\)) than that of miscanthus (16.58 MJ.kg\(^{-1}\)) [91].

Figure 74 (b) shows the maximum heat release rate at temperatures 400-600 °C. As the temperature increases, the max heat release rate increases exponentially which fits the trend of increasing temperature will increase the amount of heat liberated. From the temperatures chosen, the maximum percentage increase between each step occurs from 400-420°C, in which the heat liberated increases by 98.3% compared to the result at 400 °C. There is a drastic increase in the max heat release rate from 540 °C onwards,
in which these temperatures (540, 560, 580 and 600 °C) all exceed 4000W·g\(^{-1}\). The maximum difference in max heat release rate occurs in the final step from 580-600 °C.

![Graph showing reaction progress and max heat release rate](Figure 74: The isothermal prediction of pomace biomass combustion using AKTS software, a) isotherms showing change in reaction progress in the temperature range of 400-600 °C, b) maximum heat release rate of temperatures 400-600 °C.)
4.3.3.4. The non-isothermal prediction of pomace combustion

Figure 75 below illustrates the prediction of non-isothermal combustion of the lignocellulose material using AKTS over four different, substantially higher heating rates of 20, 50, 75 and 100 °C.min⁻¹ up to a maximum temperature of 600 °C. The reaction progress is denoted by dashed lines and the reaction rate is denoted by solid lines. This prediction profile is quantified with the rate of reaction and reaction progress for each predicted heating rate. For the 20 °C.min⁻¹ heating rate, the maximum rate of reaction was 0.00122 s⁻¹ at a temperature of 573 °C and reaction progress of approximately 0.78. At 50 °C.min⁻¹, the maximum rate of reaction was 0.00262 s⁻¹ at 498 °C, corresponding at a reaction progress of approximately 0.41. At 75 and 100 °C.min⁻¹, the maximum rates of reaction were 0.00391 and 0.00538 s⁻¹ at 394 and 404 °C, respectively. This aligned with a reaction progress of approximately 0.08. It is clear that increasing the heating rate, the maximum rate of reaction shifts upwards with every increase in temperature as shown in Figure 75. An interesting trend of this particular reaction profile is that when the heating rate is increased the alpha corresponding to the maximum rate of reaction is lowered for all of the heating rates. This shifting phenomenon is found in various other sources of biomass when under non-isothermal conditions such as the DTG profiles at four different heating rates of South African coals, thermal decomposition of corncob and rice husks under non-isothermal conditions [132-134]. Considering the non-isothermal reaction rates in comparison to the initial heating rates tested via DSC signals, the reaction rates appear to be substantially higher in the non-isothermal; predictions. This is to be expected with the higher heating rates. For example, taking the lowest heating rates in both sections, the maximum reaction rate of 0.00122 s⁻¹ at 20 °C.min⁻¹ in the non-isothermal prediction, is approximately seven times higher than that of 0.000164 s⁻¹ at 2 °C.min⁻¹. On the other hand, at the highest heating rates in both sections, the maximum reaction rate of 0.00538 s⁻¹ at 100 °C.min⁻¹ in the non-isothermal prediction, is approximately nine times higher than that of 0.000578 s⁻¹ at 8 °C.min⁻¹.
Figure 75: The non-isothermal prediction of pomace biomass combustion at higher heating rates of 25, 50, 75 and 100 °C.min\(^{-1}\) using AKTS software.

4.3.4. Validation of combustion kinetics using TGA/DTG

In order to validate the results of the kinetic parameters obtained from AKTS, a second set of thermo-analytical data in the form of TGA/DTG results was used to determine the reaction parameters and compare with the original results obtained via DSC signals. The TGA results were first imported into AKTS and then the DTG profiles were made prior to the baseline construction in order to integrate the DTG result with respect to the combustion reaction profile. The baseline types used for the TGA results were spline and tangential first point, depending on the signal.

The practical curves, their integration, and the subsequent simulated results from the TGA kinetic modelling results at different heating rates are shown in Figure 76 and 77. Like the DSC results, it showed a good match between the theoretical and kinetic modelling with \(R^2 = 0.99194\). Furthermore, the time required for the thermal
Decomposition was significantly reduced with increasing the heating rates. For example, the heating rates of 2, 4, 6 and 8 °C.min⁻¹ showed a decomposition time range of 2037-17100, 1411-8625, 891-5700 and 669-4275 s, respectively.

Figure 76: The % integrated mass derived from the TGA results of heating rates 2 (top) and 4 (bottom) °C.min⁻¹. The curve signals are blue, the integration under the curve is yellow and simulation is black.
Figure 77: The % integrated mass derived from the TGA results of heating rates 6 (top) and 8 (bottom) °C.min⁻¹. The curve signals are blue, the integration under the curve is yellow and simulation is black.

The result from the integrated DTG profiles was that on average the pomace lost 80.91 ± 3.7 wt.% of its mass when considering the four imported heating rates. The R² was found to be slightly lower than that of the DSC based model (99.194% as opposed to 99.544%), but still highly accurate, however.

The kinetic parameters were found to be similar for both the DSC and TGA results. Therefore only the reaction progress and the reaction rates of 2, 4, 6 and 8 °C.min⁻¹ in
terms of temperature were included in this section as Figure 78 (a,b) below. When considering the maximum rate of reactions, the TGA based results were found to be 0.000173, 0.000338, 0.00048, and 0.00067 s\(^{-1}\) for 2, 4, 6 and 8 °C.min\(^{-1}\). This was opposed to 0.000164, 0.000301, 0.000427, and 0.000578 s\(^{-1}\) that were reported for the DSC results of the same heating rates. It is worth noting that these maximum reaction rates that occur along the reaction progress are very similar with little deviation.

![Figure 78](image_url)

Figure 78: Shows a) the reaction progress (\(\alpha\)) and b) reaction rate versus the temperature for the pomace biomass combustion using TGA data where the coloured and dashed black curves show the practical and theoretical calculations, respectively.
4.3.5. Kinetic modelling discussion of pomace combustion (TGA/DTG)

Figure S5 (a) shows the $E_a$ calculated according to ASTM-E69 method with a value of 89.1 kJ.mol$^{-1}$. On the other hand, the FWO method showed a variation of $E_a$ during the reaction progress in the range of 84-220 kJ.mol$^{-1}$ as shown in Figure S5 (b). The differential iso-conversional method in Figure S6 was used to calculate the $E_a$ of pomace combustion, which showed a variation in the $E_a$ value in the range of 81.9-206 kJ.mol$^{-1}$. The reported average $E_a$ value of corn stover thermal decomposition with FWO and KAS models are 191.6 kJ.mol$^{-1}$ and 181.7 kJ.mol$^{-1}$, respectively [135]. The thermal decomposition of corn stock, a by-product of the agriculture harvesting of corn for human and animal feed production has been studied by Cai et al. over a range of conversion factors performed by TGA at five heating rates. As the conversion factors range from 0.05 to 0.85, the activation energies vary also from 148-473 kJ.mol$^{-1}$. However, within this variance in conversion factors, it is evident from the work, that the $E_a$ increases gradually from 148-186 kJ.mol$^{-1}$ when the conversion factor increases from 0.05 to 0.65, leading to a much sharper increase of $E_a$ from 186-473 kJ.mol$^{-1}$ as the conversion ranges between 0.65 and 0.85. The reason for this change in $E_a$ like other biomass crops is due to the different thermal kinetic behaviours of the lignocellulosic components [136].

When studying the cycle of this material, there is a clear possibility for a transition to a circular economy as the pomace is initially a spent waste material from the food and drinks sector that can be used a resource. This material is considered to have zero value since it is being sent to composting or to anaerobic digestion plants at a cost of disposal to the companies involved. Hence, we as the research body with industrially partnered links are proving the potential to turn this wasteful and valueless material into that of higher value. This can be achieved when considering its range of uses for sustainable energy production purposes as a consequence of its material properties. For example, its high calorific value for energy production, the use as biochar product as an adsorbent in wastewater treatment and the potential extraction of a bio-oil during the production of biochar. Therefore, the material which was once disposed of for composting and in some cases sent to landfill, has now been given the potential of making added-value products and may find one of many uses outlined in this study in virtually any demographic region. The future work will be studying the kinetic parameters of blackcurrant pomace pyrolysis as a more complicated process as shown from the ten-steps mechanism earlier. It is the intention of the authors and research
4.4. Conclusion

The first objective herein was to look at the physicochemical characterisation of berry pomace and its products post thermochemical conversion and determine its potential uses at the end of life to help offset the adverse environmental impacts to climate change and the circular economy. The XPS and EDX results revealed that the oxide species decreased during the formation of carbonaceous char and shifted to higher binding energy of C=O bonding in biochar basic structure due to its high inorganic content. EDX results for pomace ash showed high potassium content of 28.5wt.%, making the ash an extremely valuable fertiliser for agriculture post-combustion. Pomace biomass waste showed high higher heating value (HHV) of 21.36 MJ.kg$^{-1}$, making it a good candidate to be used in energy application compared with other biomass energy crops.

The main objective of this study was to evaluate the kinetic triplet concerning the combustion of berry pomace using thermo-analytical data such as DSC and TGA/DTG. The model was constructed utilising a model-free method using DSC, validated using TGA and both, isothermal and no-isothermal predictions were made at higher heating rates to represent a realistic scenario that would occur. Model fitting kinetics would, therefore, prove to be unreliable for the combustion of biomass sources such as pomace biomass due to the complex reaction mechanism of constituents contained within the biomass such as lignin, cellulose and hemicellulose. The selection of the differential iso-conversional model was mainly due to the fact that it allows the evaluation of activation energy, pre-exponential constant and the reaction rate at different extents of conversion and there is no pre-requisite of the reaction mechanism needed. Couple with this is that with model fitting kinetics, more than one reaction model can fit the decomposition data and it will only express one value for activation energy which has a degree of inaccuracy when considering real-world applied energy applications. The activation energies were also evaluated using the ASTM-E698 (88.60 and 89.12 kJ.mol$^{-1}$ from DSC and TGA results, respectively) and Ozawa-Flynn-
Wall methods (50-140 kJ.mol⁻¹). The R² value of the individual heating rates for DSC and TGA were 0.99544 and 0.99194, respectively. The differential iso-conversional method showed activation energy values in the range 84-197 kJ.mol⁻¹ for combustion. The AKTS combustion model was created by the authors for this study and validated numerically. This method of construction, validation, simulation, optimisation and then finally, prediction of the differential iso-conversional model using AKTS can be applied to other problematic feedstocks and domains of thermochemical conversion such as pyrolysis.

Ultimately, the present study outlines and showcases the relevance for optimised kinetic models for the evaluation of the kinetic triplet as a pre-requisite for industrial, large scale applications and also process design & modelling applications. This will become increasingly important as years go on for combustion and thermochemical research in general, as materials like biomass material will be targeted to help alleviate climate change and adhere to governmental legislation on climate change and emissions targets.
Figure S1: SEM images of pomace ash at different magnification levels using BSED.
Figure S2: EDX data of pomace biomass (a), pomace biochar (b) and pomace ash (c).
Figure S3: XPS surveys of pomace biomass (top) and pomace biochar (bottom).
Figure S4: DSC curves of the pomace biomass with different heating rates (i.e. 2, 4, 6 and 8 °C min\(^{-1}\)) under air atmosphere.
Figure S5: Shows the activation energy of the pomace biomass combustion using ASTM-E698 and FWO methods derived from the TGA results.
Figure S6: The kinetic parameters calculated with the differential iso-conversional, a) natural logarithm of the reaction rate in (s\(^{-1}\)) versus the inverse temperature, b) Ea and ln k\(_0\) derived from the TGA results.