Quality parameters for the prediction of mono- and polyunsaturated oil shelf-life

by

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I declare that the dissertation herewith submitted for the PhD Food Science degree at the University of Pretoria, has not previously been submitted by me for a degree at any other university.
ABSTRACT

QUALITY PARAMETERS FOR THE PREDICTION OF MONO- AND POLYUNSATURATED OIL SHELF-LIFE

by

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The primary objective of this investigation was to establish which oil quality parameters would be best suited in the generation of rapid predictive models to predict the shelf-life of mono- and polyunsaturated oils. A secondary objective was to establish if there is a relationship between accelerated oil stability tests (Rancimat) and shelf-life at ambient temperatures. A long-term storage trial was performed on palm-olein oil, representing monounsaturated oil and on sunflower seed oil, representing polyunsaturated oil. The pro-oxidant effect of copper was assessed by addition of copper acetate to palm-olein oil at three different levels. The synthetic antioxidant, tertiary butylhydroxyquinone (TBHQ), was evaluated by addition to sunflower seed oil at three different levels. Palm-olein was stored at 50°C and sunflower seed oil at 30°C for a period of one year. Nine oil quality parameters were measured at 11 time intervals.

Palm-olein oil parameters responded in the following ways: Free fatty acids (FFA) increased gradually for all the samples but remained within acceptable limits. However, surprisingly a slower rate of increase was found in the copper-containing samples, which could be because the FFAs formed in the copper-containing samples oxidised to further oxidation products. The peroxide values (PV) of copper-containing samples were, unexpectedly, much lower than the Control, which can be explained by the fact that in a long-term oxidation study such as this, the peroxide intermediates were probably converted to secondary, more stable oxidation products within a short time span. However, the increases in anisidine value (AV) and ultra violet absorption (UV) at 268
nm for copper-containing samples were higher than the Control as would be expected. Oxidative stability index (OSI, also known as Rancimat) and total tocopherol values for samples containing copper were significantly lower than those of the Control. Delta-tocotrienol was the most stable of the four homologues. The total volatile peak areas increased for all the samples. The pentanal peak areas particularly reflected the pro-oxidant effect of copper by their higher values in comparison to the Control. Hexanal showed higher levels in the Control than the copper-containing samples. In contrast, t,t-2,4-decadienal showed no increase in the Control, whereas the copper-containing samples showed significant increases. The t-2-hexenal values were unaffected. OSI and total tocopherols proved to be valuable indices for assessing monounsaturated oil quality, whereas PV and headspace volatiles can be misleading. AV is useful and small changes in FFA were found to be significant as indicated by its selection in the models. UV absorption is effective in the presence of pro-oxidants. Sensory evaluation confirmed the differences in shelf-life of the Control and copper-containing samples.

The important parameter changes for the sunflower oil were: FFA increased beyond acceptable limits in all the samples, which indicates that hydrolysis took place during storage. There was a lower rate of increase in samples containing TBHQ which could be because TBHQ would inhibit oxidation and thereby the contribution of intermediate secondary acids formed that would be titrated as FFA, would be lower. The protective effect of TBHQ was clearly reflected in PV and AV as the Control had higher values than the TBHQ-containing samples. Higher OSI values were found for the TBHQ-containing samples in comparison to the Control, which reflects the enhanced resistance to oxidation with increased TBHQ concentrations. The decrease in total tocopherols, as well as the homologues was slight, although the TBHQ-containing samples had consistently higher values than the Control. Marginal increases in UV 232 nm and 268 nm values were observed. The total volatiles, hexanal, and pentanal values reflected the protective effect of TBHQ as the Control generally had higher values than the TBHQ-containing samples. Changes in 2-hexenal and t,t-2,4-decadienal showed no trend. Sensory evaluation made no clear differentiation between the different treatments. OSI highlighted the effect of sample treatments correlating with PV, AV and hexanal content. The importance of small changes in FFA only became apparent during modeling.

Three types of prediction models were created by multiple regression analysis: i) Ideal
model including all the variables, ii) Practical model only including easily determined variables such as FFA, PV, OSI, UV absorbance at 232 nm and 268 nm and iii) OSI model used to correlate an accelerated test with shelf-life at ambient temperatures. OSI and FFA were important predictors as they were selected repeatedly by all models. Palm-olein models emphasised secondary oxidation products (AV and UV absorbance at 268 nm), whereas sunflower seed oil models selected primary oxidation products (PV). The preferential selection of secondary oxidation products in palm-olein oil was due to the considerable increase in oxidation reactions catalysed by copper. Antioxidant content emerged as an important predictor of sunflower seed oil shelf-life. OSI did not correlate well with shelf-life for both oil types and cannot be used on its own to predict shelf-life at ambient temperatures. It needs to be complemented by other parameters. The models developed will be applicable for practical implementation in industry to predict the shelf-life of mono- and polyunsaturated oils once additional research and refining have been done. The Practical models would be the easiest to implement, giving a useful indication of shelf-life, although the Ideal models should be more accurate.
UITTREKSEL

KWALITEITS PARAMETERS VIR DIE VOORSPELLING VAN MONO- EN POLI-ONVERSADIGDE Olie RAKLEEFTYD
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Die hoofdoel van hierdie ondersoek was om te bepaal watter oliekwaliteitsparameters geskik sou wees om vinnige voorspellingsmodelle te geneereer om die rakleeftyd van mono- en poli-onversadigde olies te beraam. ‘n Sekondêre doelwit was om te bepaal of daar ‘n verwantskap tussen die versnelde stabiliteitstoets (Rancimat) en rakleeftyd van olie by kamertemperatuur bestaan. ‘n Langtermyn opbergingsstoets met palm-olieën, as mono-onversadigde olie en sonneblomolie as poli-onversadigde olie, is onderneem. Die pro-oksidantieffek van koper is bepaal deur drie vlakke van koperasetaat by palm-olieën te voeg. Sintetiese anti-oksideermiddel, tersiêre butielhidroksiekinoon (TBHQ), se uitwerking is nagegaan deur drie vlakke by sonneblomolie te voeg. Palm-olieën is by 50°C en sonneblomolie by 30°C vir een jaar opgeberg en nege kwaliteitsparameters oor elf intervalle ontleed.

Palm-olieën se parameters het as volg gereageer: Vryvetsuurvlakke van alle monsters het geleidelik toegeneem, maar het binne aanvaarbare grense gebly. ‘n Onverwagte waarneming was die stadiger toenemtempo by die koperbevattende monsters. ‘n Moontlike verklaring is dat die vryvetsure in die koperbevattende monsters verdere oksidasie ondergaan het. Peroksiedwaardes van koperbevattende monsters was heelwat laer as die Kontrole waardes. Hierdie onverwagte tendens kan toegeskryf word aan die feit dat tydens ‘n langtermynstudie soos hierdie die peroksiedtussenprodukte moontlik vinnig na sekondêre stabiele, produkte omgeskakel word. Daarteenoor was die anisidienwaardes en ultravioletabsorpsie by 268 nm vir die koperbevattende monsters...
hoër as vir die Kontrole en bevestig dus die voorafgaande waarneming. Oksidatiewe stabiliteitsindeks (OSI, ook bekend as Rancimat) en totale tokoferolwaardes van koperbevattende monsters was betekenisvol laer as die van die Kontrole en delta-tokotriënel was die stabielste van die vier homoloë. Die totale vlugtige komponente en pentanal piekareas het die pro-oksidanteffek van koper weerspieël. Heksanal het hoër waarden getoon in die Kontrole as in die koperbevattende monsters. Dit is in teenstelling met die t,t-2,4-dekadiënal waar die Kontrole nie meetbare vlakke getoon het nie en die koperbevattende monsters beduidende toenames getoon het. Die t-2-heksenalwaarde het geen verandering ondergaan nie. OSI en totale tokoferole se waardes was waardevolle kwaliteitsindekse vir toepassing op mono-onversadigde olies, terwyl peroksiedwaarde en dampruim vlugtige komponente misleidend kan wees. Anisidenwaardes was bruikbaar en klein veranderinge in vryvetsuurvlakke was betekenisvol soos bevestig deur hulle seleksie in die modelle. Ultravioletabsorpsie analises was nuttig wanneer daar pro-oksident teenwoordig was. Sensoriese beoordeling het die verskil in rakleeftyd van die Kontrole en koperbevattende monsters bevestig.

Sonneblomolie het die volgende parameterveranderinge ondergaan: Vryvetsuurwaardes van al die monsters het toegeneem tot onaanvaarbare vlakke en bevestig dus hidrolietiese agteruitgang tydens opberging. Die beskermende invloed van TBHQ was opvallend en word heelwaarskynlik verklaar deur die vermindering in vorming van tussenproduktsure. Hierdie beskerming word ook weerspieël deur die vertraagde toename in peroksied- en anisidenwaardes teenoor die Kontrole. Hoër OSI waardes is met die TBHQ-behandeling verkry wat TBHQ se vermoë as antioksidant demonstreer. Tokoferolwaardes van olies het klein afinitye getoon en slegs marginale toename in ultravioletabsorpsie by 232 en 268 nm is waargeneem. Die totale vlugtige komponente, heksanal- en pentanalwaardes was weereens 'n weerspieëling van die anti-oksideermiddel se beskerming. Veranderinge in 2-heksenal en t,t-2,4-dekadiënal het geen patroon gevolg nie. Sensoriese beoordeling kon nie duidelike verskille tussen behandeling bevestig nie. OSI data en behandeling het goed ooreengestem en korrelasie met peroksied-, anisiden- en heksenalwaarde was positief. Die betekenis van die klein vryvetsuurwaarde veranderinge is eers tydens modellering besef.

Drie voorspellingsmodelle kon deur meerveranderlike regressie analises geskep word: i) Ideale model wat alle veranderlikes ingesluit het; ii) Praktiese model wat deur die maklik
bepaalbare veranderlikes, vryvetsuur-, peroksied-, OSI- en ultravioletabsorpsie-analises by 232 en 268 nm verkry is en iii) OSI model wat versnelde rakleeftydbepaling met rakleeftyd by kamertemperatuur gekorrelear het. OSI en vryvetsuurwaardes was uitstaande voorspellers want hulle is herhaaldelik deur deur alle modelle geselekteer. Palm-oleïen modelle het sekondêre oksidasieprodukte benadruk (anisidien- en ultravioletabsorpsie 268-waardes), terwyl sonneblomolie-modelle primêre oksidasieprodukte (peroksiedwaarde) geselekteer het. Die voorkeur seleksie van sekondêre oksidasieprodukte is as gevolg van die aansienlike toename in kopergekataliseerde reaksies. Anti-oksидеermiddelvlakke is ook as belangrike voorspeller van rakleeftyd geïdentifiseer. OSI het nie goed met rakleeftyd van beide tipe olies gekorrelear nie en dien dus nie as goeie voorspeller op sy eie, van rakleeftyd by kamertemperatuur, nie. Dit moet deur bykomende parameters ondersteun word. Die modelle wat ontwikkeld is kan prakties in die industri toegepas word om die rakleeftyd van mono- en poli-onversadigde olies te voorspel. Die Praktiese modelle kan maklik toegepas word om 'n goeie voorspelling van rakleeftyd te gee terwyl die Ideale modelle moontlik meer akkuraat sal wees.
“Challenges make you discover things about yourself that you never really knew”

(Cecily Tyson)
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Figure 29: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 7. The dependant variable is the shelf-life.

Figure 30: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 8. The dependant variable is the shelf-life.

Figure 31: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 9. The dependant variable is the shelf-life.

Figure 32: Predicted versus observed shelf-life values in weeks for palm-olein oil as determined by Model 10. The dependant variable is the shelf-life.

Figure 33: The percentage cases that fall within < - 4, - 2 to - 4, 0 to ± 2, 2 to + 4 and > +4 weeks when the jackknifing procedure had been applied.
on the Ideal, Practical and OSI models where the shelf-life was based on PV and AV values.

**Figure 34:** The percentage cases that fall within < - 4, - 2 to - 4, 0 to ± 2, 2 to + 4 and > + 4 weeks when the jackknifing procedure had been applied on the Ideal, Practical and OSI models where the shelf-life was based on the sensory evaluation.

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Figure 52: The effect of storage on the sensory evaluation of sunflower seed oil stored at 30°C for a period of 52 weeks (Option 1).

Figure 53: The effect of storage on the sensory evaluation of sunflower seed oil stored at 30°C for a period of 52 weeks. (Option 2).

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Figure 55: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 2. The dependant variable is the shelf-life.

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Figure 57: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 4. The dependant variable is the shelf-life.

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Figure 59: Predicted versus observed shelf-life values in weeks for sunflower seed oil as determined by Model 6. The dependant variable is the shelf-life.

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**Figure 66:** Percentage cases within each week category of the jackknifing results of the four models based on PV and AV values that was grouped into 3 categories namely: 0 to ±2 weeks, ±2 to ±4 weeks and more than +4 weeks and less than -4 weeks. 162

**Figure 67:** Percentage cases within each week category of the jackknifing results of the four models based on sensory evaluation that was grouped into 3 categories namely: 0 to ±2 weeks, ±2 to ±4 weeks and more than +4 weeks and less than -4 weeks. 164
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
</tr>
<tr>
<td>ANNW</td>
<td>Artificial neural network systems</td>
</tr>
<tr>
<td>AOM</td>
<td>Active oxygen method</td>
</tr>
<tr>
<td>AV</td>
<td>Anisidine value</td>
</tr>
<tr>
<td>BHA</td>
<td>Butylated hydroxyanisole</td>
</tr>
<tr>
<td>BHT</td>
<td>Butylated hydroxytoluene</td>
</tr>
<tr>
<td>COP</td>
<td>Conjugable oxidation products</td>
</tr>
<tr>
<td>CV</td>
<td>Conjugated diene value</td>
</tr>
<tr>
<td>DFA</td>
<td>Discriminant function analysis</td>
</tr>
<tr>
<td>DSF</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EVOO</td>
<td>Extra virgin olive oil</td>
</tr>
<tr>
<td>F</td>
<td>Test of significance between relationship between dependant variable and set of independent variables</td>
</tr>
<tr>
<td>FFA</td>
<td>Free fatty acids</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionisation detector</td>
</tr>
<tr>
<td>FS</td>
<td>Flavour sensory evaluation</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>HCL</td>
<td>Hollow cathode lamp</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>IP</td>
<td>Induction period</td>
</tr>
<tr>
<td>IV</td>
<td>Iodine value</td>
</tr>
<tr>
<td>KNN</td>
<td>K-nearest neighbour</td>
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<tr>
<td>MHE</td>
<td>Multiple headspace extraction</td>
</tr>
<tr>
<td>MLR</td>
<td>Multiple linear regression</td>
</tr>
<tr>
<td>ND</td>
<td>Not detected</td>
</tr>
<tr>
<td>OSI</td>
<td>Oxidative Stability Index</td>
</tr>
<tr>
<td>OV</td>
<td>Oxodiene value</td>
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<tr>
<td>PCA</td>
<td>Principal component analysis</td>
</tr>
<tr>
<td>PCR</td>
<td>Principal component regression</td>
</tr>
<tr>
<td>PCs</td>
<td>Principal components</td>
</tr>
<tr>
<td>PLS</td>
<td>Partial least squares</td>
</tr>
</tbody>
</table>
PV  Peroxide value
R\(^2\)  Square of the correlation coefficient
RBD  Refined, bleached and deodorised
SIMCA  Soft independent modelling of class analogy
TBHQ  Tertiary butylhydroxyquinone
TV  Totox value
UHT  Ultra high temperature
UV  Ultra violet absorption