

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

by

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Submitted in partial fulfilment of the requirements for the degree

PhD Food Science

Department of Food Science

Faculty of Natural and Agricultural Sciences

University of Pretoria

Pretoria

March 2003



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 RAKLEEFITYD

deur

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Die hoofdoel van hierdie ondersoek was om te bepaal watter oliekwaliteitsparameters geskik sou wees om vinnige voorspellingsmodelle te genereer om die rakleefityd 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 rakleefityd van olie by kamertemperatuur bestaan. 'n Langtermyn opbergingsstoets met palm-oleïen, as mono-onversadigde olie en sonneblomolie as poli-onversadigde olie, is onderneem. Die pro-oksidenteffek van koper is bepaal deur drie vlakke van koperasetaat by palm-oleïen te voeg. Sintetiese anti-oksidermiddel, tersiêre butielhidroksiekinoon (TBHQ), se uitwerking is nagegaan deur drie vlakke by sonneblomolie te voeg. Palm-oleïen is by 50°C en sonneblomolie by 30°C vir een jaar opgeberg en nege kwaliteitsparameters oor elf intervalle ontleed.

Palm-oleïen 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 toenametempo by die koperbevattende monsters. 'n Moontlike verklaring is dat die vryevetsure 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 stabielere, 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-tokotriënoël was die stabielste van die vier homoloë. Die totale vlugtige komponente en pentanal piekareas het die pro-oksidenteffek van koper weerspieël. Heksanal het hoër waardes getoon in die Kontrole as in die koperbevattende monsters. Dit is in teenstelling met die t,t-2,4-dekadiënaal waar die Kontrole nie meetbare vlakke getoon het nie en die koperbevattende monsters beduidende toenames getoon het. Die t-2-heksanalwaardes het geen verandering ondergaan nie. OSI en totale tokoferole se waardes was waardevolle kwaliteitsindekse vir toepassing op mono-onversadigde olies, terwyl peroksiedwaarde en dampuim vlugtige komponente misleidend kan wees. Anisidienwaardes 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 rakleef tyd 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 hidrolitiese agteruitgang tydens opberging. Die beskermende invloed van TBHQ was opvallend en word heelwaarskynlik verklaar deur die vermindering in vorming van tussenprodukture. Hierdie beskerming word ook weerspieël deur die vertraagde toename in peroksied- en anisidienwaardes teenoor die Kontrole. Hoër OSI waardes is met die TBHQ-behandeling verkry wat TBHQ se vermoë as antioksidant demonstreer. Tokoferolwaardes van olies het klein afname 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-oksiedeermiddel se beskerming. Veranderinge in 2-heksanal en t,t-2,4-dekadiënaal het geen patroon gevolg nie. Sensoriese beoordeling kon nie duidelike verskille tussen behandelings bevestig nie. OSI data en behandelings het goed ooreengestem en korrelasie met peroksied-, anisidien- en heksanalwaardes 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 rakleefitydbepaling met rakleefityd by kamertemperatuur gekorreleer 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-oksiedeermiddelvlakke is ook as belangrike voorspeller van rakleefityd geïdentifiseer. OSI het nie goed met rakleefityd van beide tipe olies gekorreleer nie en dien dus nie as goeie voorspeller op sy eie, van rakleefityd by kamertemperatuur, nie. Dit moet deur bykomende parameters ondersteun word. Die modelle wat ontwikkel is kan prakties in die industrie toegepas word om die rakleefityd van mono- en poli-onversadigde olies te voorspel. Die Praktiese modelle kan maklik toegepas word om 'n goeie voorspelling van rakleefityd 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)

ACKNOWLEDGEMENTS

The author would like to express her sincere gratitude and appreciation to the people and organisations that provided assistance and encouragement during this study:

I would like to thank my supervisor Prof JRN Taylor for his constructive criticism, ongoing encouragement and faith shown in me, along with his kind persistence in seeing this study reach its conclusion.

To my co-supervisor, Dr LM du Plessis, without whose encouragement I would not have attempted this. Thank you for your hours of discussion, calmness and constant support.

Dr PJ van Niekerk for invaluable help and advice on the statistical analysis and modelling.

CSIR Bio/Chemtek's Director and Programme Managers for the funding provided, time awarded and encouragement during this project.

Friends and colleagues at CSIR Bio/Chemtek that always listened, remained patient and gave valuable advice and support.

Michéle Enslin for all the help and patience in putting it together into this format.

To my family along with all my friends that remained positive and supportive towards me during this challenging period of my life.

My fiancée, Fergus, for always being there with encouragement, understanding, loads of patience and love (and endless cups of tea!).

Without all the encouragement and support, this would have been so much harder.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
ANNW	Artificial neural network systems
AOM	Active oxygen method
AV	Anisidine value
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
COP	Conjugable oxidation products
CV	Conjugated diene value
DFA	Discriminant function analysis
DSF	Differential scanning calorimetry
EVOO	Extra virgin olive oil
F	Test of significance between relationship between dependant variable and set of independent variables
FFA	Free fatty acids
FID	Flame ionisation detector
FS	Flavour sensory evaluation
GC	Gas chromatography
HCL	Hollow cathode lamp
HPLC	High performance liquid chromatography
IP	Induction period
IV	Iodine value
KNN	K-nearest neighbour
MHE	Multiple headspace extraction
MLR	Multiple linear regression
ND	Not detected
OSI	Oxidative Stability Index
OV	Oxodiene value
PCA	Principal component analysis
PCR	Principal component regression
PCs	Principal components
PLS	Partial least squares

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