Exploding the myth - NZ Extra Virgin Olive Oil is an ideal frying oil

Laurence Eyres, Marie Wong, Selee Cho, Mike Cundy

Background

The New Zealand olive oil industry has been quietly evolving over the last decade. By global standards the annual output is small at around 300 tonne p.a. This contrasts with the Australian output of extra virgin oil of around 30,000 tonnes p.a. The small output in New Zealand results in high prices to the end user precluding its use in commercial operations.

Frying oils should have a combination of nutritional merit and heat stability (Drummond, 2007). Australasian olive oil is of exceptionally high quality and regularly wins awards and medals domestically and overseas. Despite its low saturated fat content, great flavour and antioxidant content (polyphenols) there is still widespread resistance to its use in domestic frying applications. The public persists in using refined, bleached and deodorised (RBD) highly unsaturated oils sold in supermarkets in clear plastic bottles which can lead to a high peroxide value before even opening the bottle.

There are growing health concerns about oxidised and heat abused oils in human nutrition over contaminants such as toxic aldehydes (Guillen, 2012) in used oils and 3-MCPD (3-monochloropropane-1,2-diol) and GE (glycidyl esters) occurring in fresh RBD oils. This research project set out to evaluate and compare the stability of extra virgin olive oils and to compare the levels of breakdown products after cooking for set periods.

There is also an old myth which abounds on the internet and in populist magazines that one cannot fry with olive oil in the home as it smokes badly and produces toxic compounds on heating. This project was designed to investigate this myth.

The traditional way of evaluating an oil for frying applications was to look at the smoke point. Many marketing documents made spurious and erroneous claims concerning high smoke points when no standard analyses had been carried out. This project determined that the smoke point is only a minor part of a systematic evaluation of stability.

Introduction

Forty-five years ago, New Zealand olive oil was virtually unknown to the local consumers. Animal fats commanded the major market share and heart disease was endemic. Since then imports of all vegetable oils have grown, and olive oil has become a staple on the market shelves. Ninety percent of the olive oil sold in New Zealand (30,000 tonne) is via the supermarkets and is imported from mainly European countries such as Spain, Greece and Italy. A great deal of the olive oil is not good quality and is also not fresh. The imported oil is seldom tested for quality or authenticity so the public could be getting poor service in terms of olive oil supply and the image of genuine extra virgin olive oil suffers.

For extra virgin olive oil (EVOO), there are international quality standards such as Codex Alimentarius, Commission Regulation (EU) no.2568/91, International Oil Council (IOC) and Standards Australia AS 5264-2011 which are used for classifying the various classes of olive oil according to its chemical (Table 1) and organoleptic quality (Codex Alimentarius, 2017; European Commission, 2002; International Olive Council, 2006; Standards Australia, 2011). New Zealand, in 2011, did not choose to adopt the modern Australian standard for extra virgin olive oil which clearly defines the standards for authentic olive oils, instead New Zealand has remained with the Codex and IOC standards which have very broad ranges for various quality standards allowing lesser quality olive oils also to be labelled as the highest quality olive oil.

Table 1. Quality standards for % free fatty acid (%FFA) and peroxide value (PV) for different types of olive oil (Codex Alimentarius, 2017; European Commission, 2002; International Olive Council, 2006; Standards Australia, 2011).

Category	Free fatty acid (% as oleic acid)	Peroxide value (mEq/kg)
Extra virgin olive oil	≤0.8	≤20
Virgin olive oil	≤2.0	≤20
Olive oil[a]	≤1.0	≤15
Refined olive oil	≤0.3	≤5

[a] *A combination of virgin and refined olive oils*

There are many different brands and many different quality grades available at surprisingly low prices in the supermarkets. A considerable portion of the virgin olive oils sampled were of poor quality, had high acidity and subsequently had low smoke points (Eyres 2015). This has led to the commonly held view that all olive oils are unsuitable for frying and high temperature cooking. EVOO of high quality is abundant in monounsaturated fatty acids (MUFAs) and in phenolic compounds such as polyphenols, tocopherols (vitamin E), and squalene. Naturally present phenolic compounds not only act as an antioxidant but are responsible for the positive organoleptic properties such as bitterness, pungency, astringency and green-leaf aroma of the EVOO. These naturally occurring compositional characteristics, as well as the distinctive, high quality aroma and flavour of EVOO are well preserved through minimal mechanical processing of washing, crushing, malaxing, decantation and separation without any further processing (Edwards, 2007).

Figure 1. The Testo 270 monitor

Frying with oils

Deep fat frying and shallow pan frying are very common ways of cooking and dehydrating a wide range of foods at temperatures from 170-230°C. Deep frying is generally carried out between 170-180°C and shallow pan frying tends to be uncontrolled with temperatures between 180-230°C. Probably the most common fried snack products are potato and corn chips. Potatoes are cooked from a moisture content of 80% down to 1.5%. The fat contents of fried foods vary from around 35% in potato chips to 7-14% in French fries. The control and disposal of over-used cooking oil presents several problems. Not only are there environmental issues and health issues to consider, the assessment of the degree of degradation traditionally requires tedious and laborious chemical analysis procedures. Once the degree of degradation is established, the disposal or recycling of the used cooking oil presents another huge dilemma for disposal, but it does have a potential use in biodiesel.

Heating of oils to frying temperatures is widely practiced in many industrial and culinary processes. It is known, however, that oils degrade with heating and that this degradation is greater when the heating temperature is higher and when the time spent at these temperatures is longer. During frying many complex chemical processes occur. Hydrolysis occurs by reaction of the triglycerides with any moisture present, producing free fatty acids. Oxidation and bond cleavage also yield materials which are analysed as acidic components. Oxidation, polymerisation, conjugation and isomerisation all happen, producing a multi-component mixture of breakdown products which lead to a degrading of colour (darkening of the oil) and an increase in viscosity. The nature and concentration of the compounds present in the oil can be monitored as total polar materials (TPM) which is a consequence of the thermal and oxidative degradation of the lipids and other compounds such as sterols during heating (Dutta, 2007). These TPMs are a matter of great interest as some of these compounds are toxic and can be ingested directly from the degraded oil or through fried food. Some European countries have set the maximum amount of TPM in the oil at 25%. Many test methods over the years have been used to evaluate the stability of oils for frying and their resultant shelf life. The most relevant parameter after years of research has been found to be the amount of total polar material in the oil (TPM) (Fritsch, 1981). The Testo 270 monitor is a quick and easy to use hand-held tester which is suitable for the measurement of TPM in the field or in the laboratory (Figure 1) (Testo, 2019).

Analytical methods used in this project

% Free fatty acids (FFA), p-Anisidine value (AV), smoke point and fatty acid composition were determined using AOCS standard methods used regularly in laboratories (AOCS, 2009). The Rancimat method (AOCS Cd 12b-92: Metrohm, Switzerland) for predicting stability is now a well-accepted automated method, replacing the old oxidation stability evaluation (OSI) (AOCS, 2009). The Testo apparatus (Testo, Germany) was used for total polar material TPM). Total phenolics were determined using the Folin-Ciocalteu method using caffeic acid for the standard curve based on the method by Singleton and Rossi (1965). The smoke point of the oils was determined at Flinders Cook, Auckland, using the AOCS Cc 9a-48 method.

Oils Tested

Extra virgin olive oils were selected from winners of the Auckland A&P Royal Easter Show competition 2018. Other olive oils were chosen from a local supermarket for comparison, including an Australian and a European extra virgin oil and a popular canola oil (Table 2.). The New Zealand EVOOs had already met the Olives NZ standard for extra virgin olive oil prior to entering the Royal Easter Show competition, % FFA <0.5% and PV < 15 mEq/kg.

Table 2. The origins, olive cultivars, press dates and best before dates for each EVOO or canola oil sample

Sample	Origin of olive oil/canola oil	Cultivar	Press date	Best before date
NZ 1	Mangonui	'Frantoio'	May 2017	May 2019
NZ 2	Waiheke Island	NI	May 2017	May 2019
NZ 3	Martinborough	'Barnea'	June 2017	June 2019
NZ 4	Wellsford	NI	May 2017	May 2019
IT	Italy	NI	April 2017	April 2019
AU	Australia	NI	October 2017	October 2019
CAN	Canola (refined)	NI	-	February 2020

NI – not identified

Simulated Frying

To simulate extended frying the oils were heated to 180 ± 5°C for 10 hours, during heating samples of the oil were tested every two hours for p-Anisidine value and total polar material (TPM).

Table 3. Fatty acid composition (%) evaluated in EVOO samples and canola oil.

Sample	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0
NZ 1	12.6	0.7	1.8	74.7	5.9	0.5	0.3	0.3	0.1
NZ 2	9.8	0.5	2.0	78.3	5.4	0.7	0.3	0.3	0.1
NZ 3	8.0	0.3	2.1	79.4	6.8	0.7	0.3	0.3	0.1
NZ 4	11.4	0.7	1.7	76.6	5.0	0.7	0.3	0.4	0.1
AU	11.4	0.7	2.4	76.2	4.8	0.7	0.4	0.3	0.1
IT	10.4	0.7	3.0	77.0	4.8	0.7	0.4	0.3	0.1
CAN	4.3	0.5	1.8	58.2	20.0	7.4	0.5	1.1	0.3

Results

Initial assessment of oils

The fatty acid composition (% of total fatty acids present) of the EVOOs and the canola oil was determined by GC and are reported for each oil in Table 3.

The oil samples were first evaluated for their oxidative stability. The induction time for the oil was measured using the Rancimat method. Induction time was expressed in hours, which indicated the oxidative stability of the oil; long induction times indicate an oil with good oxidative stability. Total phenolic contents of EVOO samples were also determined (Table 4). For the EVOOs, the shortest and longest induction times were found in the oils with the lowest and highest concentrations of total phenolics, respectively. The refined canola oil was found to have a similar induction time as NZ 3 EVOO. However, canola oil contained the lowest total phenolic content of 48.8 mg per kg of oil, as the phenolic compounds were removed during refining. Hence, the oxidative stability in the canola oil sample was not due to phenolic concentration but due to a removal of other components which can induce oxidation such as free fatty acids, phospholipids, volatiles and other minor components.

Table 4. Induction time (h) obtained from Rancimat and total phenolic contents of EVOOs and canola oil. The values are means of triplicate Rancimat measurements and totol phenolic content (mean+-SEM, n=3)

Sample	Induction time (h)	Total phenolic content (mg/kg oil)
NZ 1	48.5 ± 0.8	948.1 ± 0.0
NZ 2	16.2 ± 0.5	448.8 ± 1.3
NZ 3	21.2 ± 0.6	670.8 ± 0.0
NZ 4	36.0 ± 0.9	938.7 ± 9.4
AU	33.5 ± 0.5	812.8 ± 12.9
IT	32.1 ± 0.4	714.0 ± 0.0
CAN	21.3 ± 0.3	48.8 ± 3.9

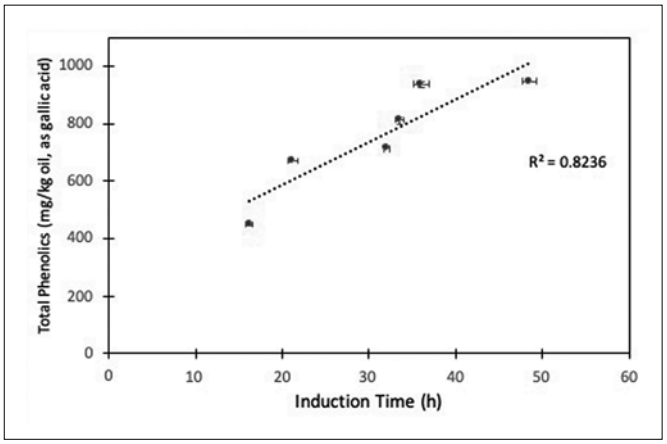

Figure 2. Correlation between total phenolics and induction time for EVOO samples. (mean values ± standard errors, n = 3)

A strong correlation was found between Rancimat induction time and the concentration of total phenolics present in EVOOs (R2 = 0.82) (Figure 2), which agrees with other previous research (Aparicio, Roda, Albi, & Gutiérrez, 1999; Silva et al., 2010). A strong positive correlation could be the result of radical scavenging activity of phenolic compounds, protecting oil under accelerated oxidation conditions.

Table 5. %Free fatty acid of EVOO (w/w as % oleic acid) and smoke point of EVOOs and canola oil. The % FFA values are means ± SEM for n=3.

Sample	% FFA (% Oleic acid)	Smoke point (°C)
NZ 1	0.20 ± 0.02	208
NZ 2	0.10 ± 0.04	206
NZ 3	0.20 ± 0.03	196
NZ 4	0.10 ± 0.02	206
AU	0.30 ± 0.02	192
IT	0.50 ± 0.00	194
CAN	0.10 ± 0.02	228

The % FFA (as oleic acid) and the smoke point of the EVOOs and canola oil are presented in Table 5. The values of %FFA for all the EVOOs and refined canola oil were below the International Olive Council upper limit of 0.8% (as oleic acid) for extra virgin olive oil and 0.2% for refined oil. The smoke point is defined as the temperature at which smoking is first detected (Karl, 2007). The %FFA is strongly correlated with the oils' smoke point. The greater the extent of hydrolysis of the triglycerides the more free fatty acids present which leads to early detection of smoke at lower temperatures.

Simulated Frying

To simulate frying conditions the oils were heated for 10 hours at 180°C and tested every two hours. The increase in TPMs with heating was observed in all oils as shown in Figure 3. The p-Anisidine value (AV) monitored during simulated frying for the EVOOs and the canola oil are shown in Figure 4. For all oils the AV increased with heating time though the rate of increase varied for each oil. The initial AV value for

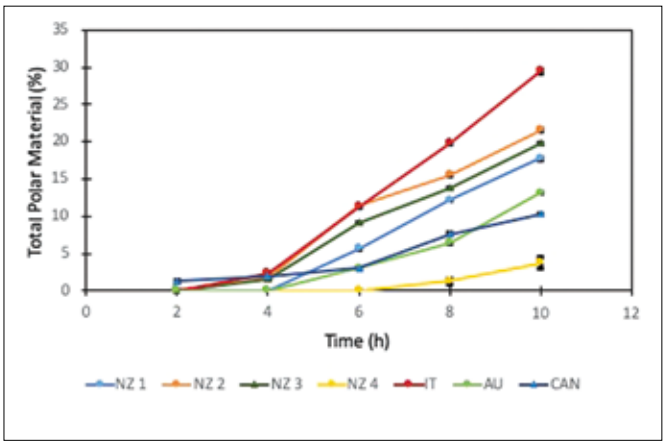

Figure 3. Increase in total polar materials (TPM %) in EVOOs and canola oil, as measured by a Testo meter during heating at 180 ± 5°C (mean values ± SEM, n = 4)

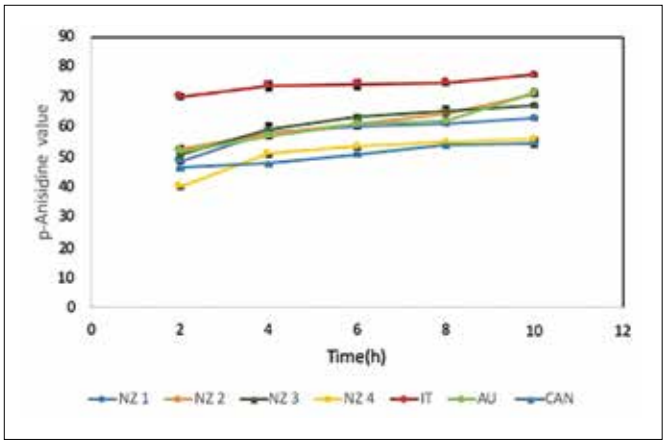

Figure 4. Increase in p-Anisidine value (AV) in EVOOs and canola oil during heating at 180 ± 5°C (mean values ± SEM, n = 3

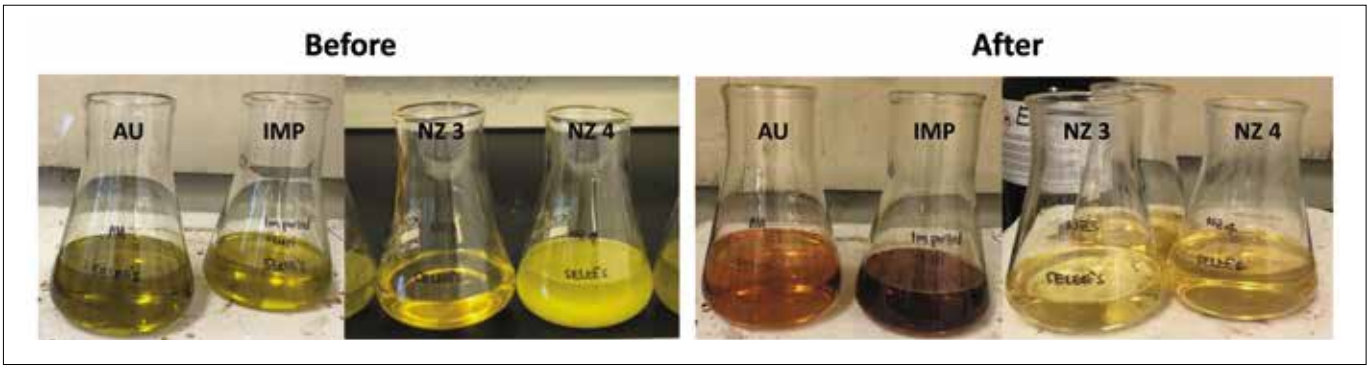

Figure 5. Samples of EVOOs before and after simulated frying at 180 ± 5°C for 10 hours. AU – Australia, IMP – Italy, NZ 3 – New Zealand 3, NZ 4 – New Zealand 4

Table 6. % Free fatty acids of EVOOs and canola oil before and after 10 hours simulated frying at 180 ± 5°C (mean values ± SEM).

Sample	Initial % FFA (% as oleic acid)	Final % FFA (% as oleic acid)
NZ 1	0.20 ± 0.02	0.39 ± 0.03
NZ 2	0.10 ± 0.04	0.50 ± 0.04
NZ 3	0.20 ± 0.03	0.45 ± 0.03
NZ 4	0.10 ± 0.02	0.22 ± 0.07
AU	0.30 ± 0.02	0.68 ± 0.02
IT	0.50 ± 0.00	0.70 ± 0.00
CAN	0.10 ± 0.02	0.32 ± 0.02

the Italian EVOO was initially high and it remained higher than all other oils. All oils darkened in colour after 10 hours of heating (Figure 5). The initial and final % free fatty acids of the oils after 10 hours heating are presented in Table 6, and show increased values in all oils.

Discussion

The EVOOs and canola oil tested showed good oxidative stability and also stability to frying. The Rancimat oxidative stability test showed good correlation with the level of polyphenols in the oil. As these polyphenols are also reported to have health benefits this is a double advantage for EVOO. The New Zealand EVOOs with the longest induction time and highest total phenolics also performed the best after simulated frying with lower levels of TPMs and p-Anisidine values. Some countries in Europe have strict legislation covering the use of frying oils – most of them specify a TPM content less than 25%. A TPM level of 24 - 27% is considered to be an unacceptable level for

consumption. The Italian EVOO was the only oil to be unacceptable in terms of TPM after 10 hours of heating.

Smoke point is always quoted as the major criteria for choosing a frying oil but this and other studies have shown that the initial smoke point is not correlated at all with the lifetime stability of a cooking oil and should not be the only measure to evaluate the suitability of any oil for frying. Even though the initial smoke point for a frying oil needs to be high (>190 degrees) there are other factors that influence the oil's stability, including the fatty acid composition and the presence of minor components such as phenolics and tocopherols which act as stable antioxidants. Evaluation of several different vegetable oils in a comprehensive study by De Alzaa et al. (2018) found that EVOO was the most stable frying oil and produced the least polar material on prolonged heating.

Conclusions

The recommended criteria for a stable EVOO for frying are thus:

- Initial %FFA<0.2% (w/w as oleic acid), with a corresponding high smoke point >190°C.
- PV< 5.0 mEq/kg
- Induction time in Rancimat > 15 hours.
- TPC after 8 hours heating at 180°C <25%
- p-Anisidine value after 8hours at 180°C <70

The project concluded that quality extra virgin olive oil, that also meets the Olives NZ approval tick, is the best frying oil for use in the home from a stability and health viewpoint. This cannot be concluded for lesser quality imported olive oils which do indeed smoke in the kitchen.

This paper is based on a project completed by a Massey University final year Bachelor of Food Technology with Honours student, Selee Cho in 2018.

The project was sponsored by the NZIC Oils and Fats Specialist Group and the Auckland Agricultural, Pastoral and Industrial Shows Board, who are the organisers of the annual Royal Easter Show Olive Oil competition.

Associate Professor Marie Wong is in the School of Food & Advanced Technology, SF&AT Albany Campus Leader, Massey University, Albany Campus, Auckland.

Laurence Eyres of ECG Consulting is Chairman of the NZIC Oils and Fats Specialist Group.

Mike Cundy is the convener of the Royal Easter Show Olive Oil competition.

Selee Cho is a graduate of a Bachelor of Food Technology (Hons) from Massey University.

References

AOCS. (2009). Official methods and recommended practices of the American Oil Chemists' Society. Champaign: American Oil Chemists' Society.

Aparicio, R., Roda, L., Albi, M. A., & Gutiérrez, F. (1999). Effect of various compounds on virgin olive oil stability measured by Rancimat. *Journal of Agricultural and Food Chemistry,* 47(10), 4150-4155.

Codex Alimentarius. (2017). Proposed draft revision to the Standard for Olive Oils and Olive Pomace Oils (CODEX STAN 33-1981): Revision of the Limit for Campesterol. Retrieved 06/09/2017 from http://www.fao.org/fao-who-codexalimentarius/en/

De Alzaa, F., Guillaume, C. and Ravetti, L. (2018). Evaluation of Chemical and Physical Changes in Different Commercial Oils during Heating. *Acta Scientific Nutritional Health.* 2(6): 2-11.

Drummond, L. (2007). Deep-frying Mediums in New Zealand. In O'Connor, C.J. & Eyres, L. (Eds.), Handbook of Australasian edible oils. Oils and Fats Specialist Group of NZIC. Auckland.

Dutta, P.C., Przybylski, R., Eskin, M.N.A., Appelqvist, L. 2007. Formation, Analysis, and Health Effects of Oxidized Sterols in Frying Fat. In Erickson, M.D (ed) Deep Frying: Chemistry, Nutrition, and Practical Applications. Academic and AOCS Press, p 87-110.

Edwards, M. The Development of the New Zealand Extra Virgin Olive Industry (2007). In O'Connor, C.J. & Eyres, L. (Eds.), Handbook of Australasian edible oils. Oils and Fats Specialist Group of NZIC. Auckland.

European Commission. (2002). No 796/2002 of 6 May 2002 amending Regulation (EEC) No 2568/91 on the characteristics of olive oil and olive pomace oil and on the relevant methods of analysis and the additional notes in the Annex to Council Regulation (EEC) No 2658/87 on the tariff and statistical nomenclature and on the Common Customs Tariff. Retrieved 06/09/2017 from http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=LEGISSUM:l11054

Eyres, L. (2015). Frying oils: selection, smoke points and potential deleterious effects for health, *Food New Zealand,* February: 30-31.

Fritsch, C.W. (1981) Measurements of Frying Fat Determination: A Brief Review. *Journal of American Oil Chemists' Society.* 58(3):272–274.

Guillén, M.D., Uriarte, P.S. (2012). Aldehydes contained in edible oils of a very different nature after prolonged heating at frying temperature: Presence of toxic oxygenated α, β unsaturated aldehydes. *Food Chemistry* 131 (3): 915-926.

International Olive Council. (2006). Trade standard applying to olive oils and olive-pomace oils. Retrieved 01/09/2017 from http://www.internationaloliveoil.org

Karl, D. (2007). Methods of Analysis- A Brief Introduction. In O'Connor, C.J. & Eyres, L. (Eds.), Handbook of Australasian edible oils. Oils and Fats Specialist Group of NZIC. Auckland.

Silva, L., Pinto, J., Carrola, J., Paiva-Martins, F. (2010). Oxidative stability of olive oil after food processing and comparison with other vegetable oils. *Food Chemistry*, 121(4):1177-1187.

Singleton, V.L., Rossi, J.A. 1965. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *American Journal of Oenology and Viticulture.* 16:144-158.

Standards Australia (2011) Olive Oils and olive-pomace oils AS5264. July 2011.

Testo (2019) www.testo.com.