



Towards a wicking rapid test for rejection assessment of reused fried oils: Results and analysis for extra virgin olive oil



John S. Lioumbas, Angelos Zamanis, Thodoris D. Karapantsios *

Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, University Box 116, 541 24 Thessaloniki, Greece

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ABSTRACT

This work investigates the potential of developing a rapid test based on wicking of oil into paper for determining whether a reused frying oil is to be rejected. To achieve this goal, wicking patterns (oil penetration rate and oil front shape versus time) of both fresh and prolonged fried extra virgin olive oil are optically registered at six different paper stripes. Four of them are double-ply towel papers whereas the other two are single-ply chromatographic papers. Wicking tests are performed at 20 °C and 30 °C. It is shown that the type of paper affects seriously the wicking patterns. Double-ply papers present high oil penetration rates but very irregular oil front shapes whereas single-ply papers yield lower oil penetration rates but pretty flat oil fronts. Furthermore, it is found that only under certain conditions the penetration rates obey the well known Lucas–Washburn equation. A discussion is made on the phenomena that take place during wicking of oil into paper which may cause deviations from the Lucas–Washburn equation. A semi-empirical model is proposed to describe the above deviations by incorporating the effect of time evolving pore sizes.

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1. Introduction

The intense and complex heat and mass transfer processes during deep fat frying result in significant oil degradation (Bouchon et al., 2003) which imposes oil replenishment in sequential frying batches. The determination of the exact instant that frying oil must be replenished is a major concern for avoiding possible health risks (Bansal et al., 2010a) but also for estimating the cost of fried foods in food industry and catering applications (Kress-Rogers et al., 1990). The official analytical procedures used in laboratories to assess the quality of prolonged (or repeated) fried oils are very accurate but are also time consuming, expensive and cannot be used on the spot in industrial or catering applications. Hence, use of rapid tests is gaining attention in actual applications where there is need for quick evaluation of whether the total polar compound content of the oil has surpassed 25% by mass and so has to be discarded according to international laws (Bansal et al., 2010b; Paul and Mittal, 1997). A rapid test should exhibit the following characteristics: (i) correlate well with official analytical methods, (ii) provide an objective index, (iii) quantify the degree of oil degradation, (iv) be easy and inexpensive to use, (v) be independent from the nature of frying oil, (vi) have no influence from the fried food, and (vii) be safe to use in food production area (no toxic chemical, no glassware, etc.) (Gertz, 2000).

Gupta (2005) and Bansal et al. (2010a) in a comprehensive review categorized the existing rapid tests on those based on measuring physical parameters (i.e. color, dielectric constant and viscosity) and those based on measuring chemical parameters (i.e. total polar compounds, oxidized/free fatty acids and carbonyl compounds). Using an analytical laboratory method (size exclusion chromatography, HPSEC) Gertz (2000) determined polar materials, polymerized triglycerides and acid value of 150 different samples of deteriorated oil. He employed these results as reference to compare with and evaluate different commercial rapid tests based on the determination of chemical parameters (alkali colour number: *Fritest*®, and oxidation products: *Oxitest*®) and physical parameters (dielectric constant: *Foodoil Sensor*™ - *FOST*™, Northern Instruments Corp., and relative viscosity and density: *Fri-Check*®). He found that the tests based on chemical parameters depend highly on the particular frying conditions (e.g. type of oil and food) and give poor correlation with analytical methods ($r^2 \sim 0.45$). On the contrary, physical parameters show good correlation with analytical methods ($r^2 \sim 0.894$). Marmesat et al. (2007) evaluated also the performance of several commercially available rapid tests in a significant number of fried oil samples (i.e. 105 samples). These rapid tests were based on changes of either oil physical properties (i.e. viscosity – *Viscofrit*®, dielectric constant – *FOST*™) or oil chemical properties (i.e. carbonyl compounds – *Fritest*®, total amount of oxidized compounds – *Oxitest*®) during frying. Similarly to Gertz (2000) these authors also observed that rapid tests based on

* Corresponding author. Tel./fax: +30 2310997772.

E-mail address: [karapant@chem.auth.gr](mailto:karpant@chem.auth.gr) (T.D. Karapantsios).

physical properties give better results than those based on chemical properties.

Comparison among rapid tests based on physical parameters demonstrate that measuring the dielectric constant suffers from the tedious step to filter every sample before each test in order to remove traces of salt, water and minerals that enhance polarity (Gertz, 2000). Furthermore, Gertz (2000) showed that viscosity can be considered as a reliable physical parameter for rapid determination of oil quality, since the results obtained with *Fri-Check*[®], are correlated very well ($r^2 = 0.917$) with the concentrations of polar materials and polymerized triglycerides. This was confirmed by Marmesat et al. (2007) who also reported that viscosity is a more accurate quality indicator than any other physical property. Very recently Osawa et al. (2012) used 59 different frying oil samples to evaluate the effectiveness of rapid tests based on oil's physical properties (viscosity tests: *Viscofrit*[®] and *Fri-Check*[®]; dielectric constant test: *Testo 265*). These authors argued that tests based on dielectric constant demand extremely careful calibration (i.e. by using an oil of well defined properties) before measurement and concluded, too, that viscosity tests are superior.

The above indicate that viscosity is a promising physical property to determine oil degradation in rapid tests. Two are the commercially known rapid tests that use viscosity as the examined parameter: i.e. *Fri-Check*[®] and *Viscofrit*[®]. *Fri-Check*[®] consists of an electronic system that measures the time needed for a piston-like body to free-fall inside a steel tube filled with oil. The fall time, which depends on oil's viscosity, yields automatically the polar compounds percentage, through a correlation function programmed in the software by the manufacturer (Stier, 2004). Testing requires 15 ml oil samples and lasts about 10 min because of several thermal regulation steps to a final sample temperature of 52 °C (Osawa et al., 2012). Although this device is valuable for rough estimations, its outcome may be seriously affected by dispersed particulates in the oil (unless filtered), poor temperature uniformity in the oil and end-effects due to the short length of the test tube. In addition, it does not allow adjustment to new types of oil besides those already incorporated in the correlation

function and is rather complicated for techno-phobic people working in small scale catering enterprises and domestic users. On the other hand, *Viscofrit*[®] is based on the time spent to empty a funnel-like cone filled with the frying oil (Marmesat et al., 2007). It is simpler and faster than *Fri-Check*[®], as the analysis takes less than 2 min but it requires approximately 30 ml of oil for a single test whereas calibration and oil filtration are needed before each test (since the presence of food particles in the oil may seriously affect measurements) (Marmesat et al., 2007). In addition, a good knowledge of oil temperature is needed (preferably between 20 °C and 30 °C) in order to interpret correctly the measurements.

Paper-based microfluidic sensors are emerging as a new technology for rapid tests in medical diagnostics for the developing world, where low cost, simplicity but also accurate results are essential (Martinez et al., 2010). Paper is already used extensively in analytical and clinical chemistry as a wicking medium (Martinez et al., 2010) because it is relatively cheap and abundant, sustainable, disposable, and easy to use, store, transport and modify. Paper has the unique property of being able to move fluids by capillary action without the need for power and effect separation of components in mixtures (Hossain et al., 2009).

Wicking of oil into paper is not a popular subject in literature. The vast majority of studies refer to wicking of aqueous solutions on porous solid matrices while a few other studies use alkanes as wicking liquids to maximize wettability of the solid (Van Oss et al., 1992). In our lab we have employed wicking experiments of alkanes into thin starch films in order to determine the effective pore size of these starch sheets (Kalogianni et al., 2004). Systematic efforts on wicking of non-polar liquids such as oil appear in printing applications (Daniel and Berg, 2006), in fibrous materials (e.g. candles and textiles) related applications (Patnaik et al., 2006) and in soil science (Ridgway et al., 2011; Chung et al., 2012). To our knowledge there is no study concerning the development of a paper based wicking rapid test for the determination of frying oil quality. This is indeed the objective of this work: to explore the potential of using thin paper sheets as a wicking medium to swiftly and accurately discriminate fresh from heavily fried oil. In

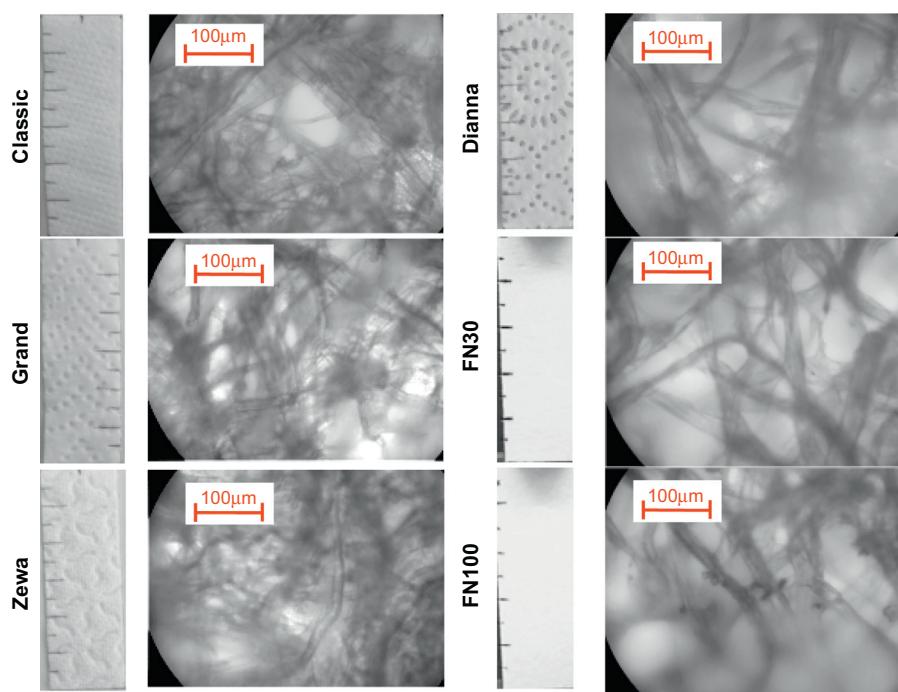


Fig. 1. Macroscopic and microscopic views of the wicking papers used in this study.

Table 1

Physical properties of olive oil. Accuracy of viscosity and interfacial tension measurements: $\pm 0.75\%$ and 0.5% respectively.

	Fresh oil		Prolonged fried oil	
	20 °C	30 °C	20 °C	30 °C
Dynamic viscosity, μ (mPa s)	85.0	57	110	73.8
Surface tension, γ (mN/m)	30.8	30.8	30.0	30.0

this respect, experimental parameters that control oil wicking into paper are analyzed and optimum conditions for reliable performance are identified. Furthermore, a semi-empirical model is proposed to describe measurements speculating on a decreasing paper pore size during wicking.

2. Materials and methods

2.1. Frying protocol

Repeated frying experiments are conducted in order to produce heavily deteriorated oil (prolonged fried oil). The conditions of the repeated frying experiments were selected in such a way to allow a considerable (also realistic for industrial and catering applications) change in the chemical profile of the frying medium.

The schematic layout of the setup used for frying experiments can be found elsewhere (Fig. 1 at Lioumbas et al., 2012a). Frying was performed in a commercial fryer (DELONGHI, F885-DIVA) with

a maximum oil capacity of 1.9 L and nominal power of 1800 W. During the frying experiments, it was considered important to expose all potato sticks to the same conditions in the fryer (i.e. uniform oil temperature across the fryer). A controller (adjusted to a small gain to avoid temperature overshoots, BTC 9060, Brainchild Electronic, UK) reduced the delivered power to the fryer inversely proportional to the instantaneous temperature difference from the set point (oil temperature: 180 °C, accuracy ± 0.1 °C). The frying series started with 1.9 L of fresh oil in the fryer. The volume of oil, L_{oil} , decreased after every 10 batches, due to sampling of oil but also oil absorption from the potatoes. The oil was not replenished between frying batches so in order to keep the frying load constant through the 40 batches (frying load: 1/7 kg_{potatoes}/L_{oil}), the mass of the potatoes in the fryer was reduced accordingly. Forty repeated batches constitute a tradition for domestic users in Greece to discard the fried olive oil because it gets considerably dark and turbid compared to fresh oil (Blekas et al., 2011). The prolonged fried oil used in the wicking tests is collected after the 40th batch of repeated frying batches. Each frying batch lasted 5 min. The total time that the oil was kept at elevated temperatures, was 5 h (continuous) including the time needed for heating up the oil before frying and the time in-between frying batches.

2.2. Oil and paper properties

Extra virgin olive oil is used as a frying medium (donated by Elais S.A., Greece). Olive oil was chosen as one of the most common and favorable fat for domestic and catering applications in

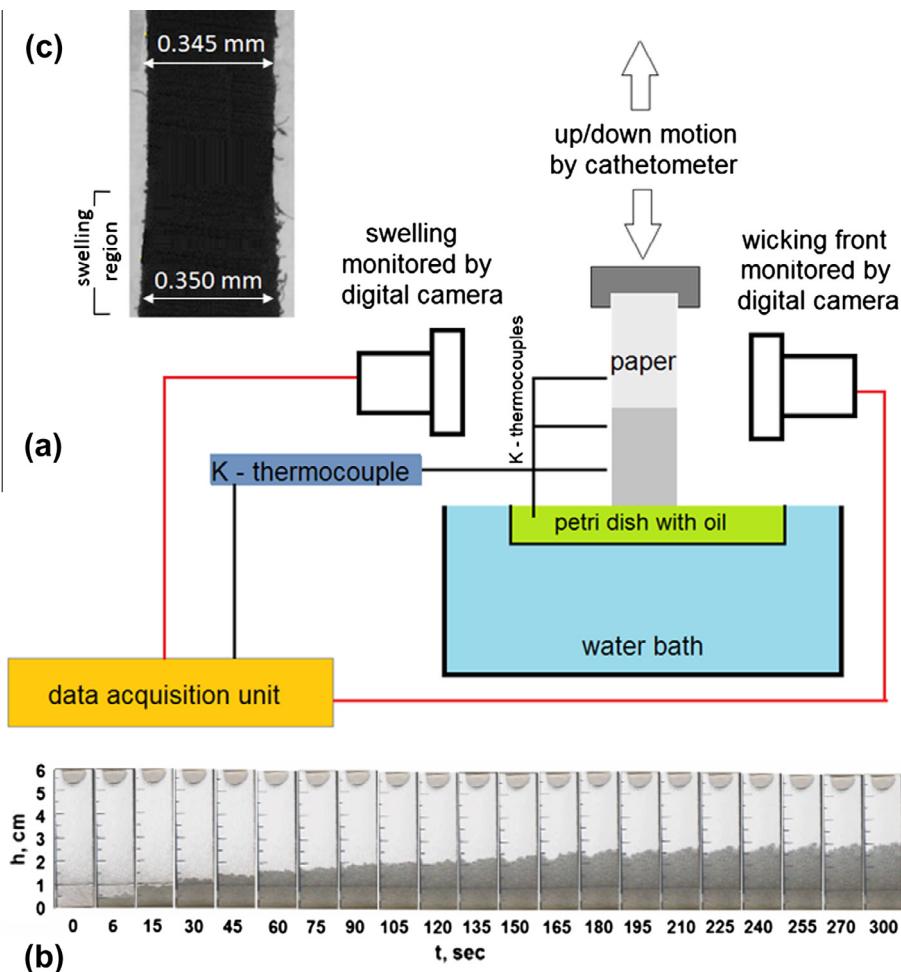


Fig. 2. (a) Schematic layout of the experimental configuration; (b) image sequence of wicking fronts of fresh oil into Classic paper (c) typical swelling profile (side view) of FN30 chromatographic paper during wicking.

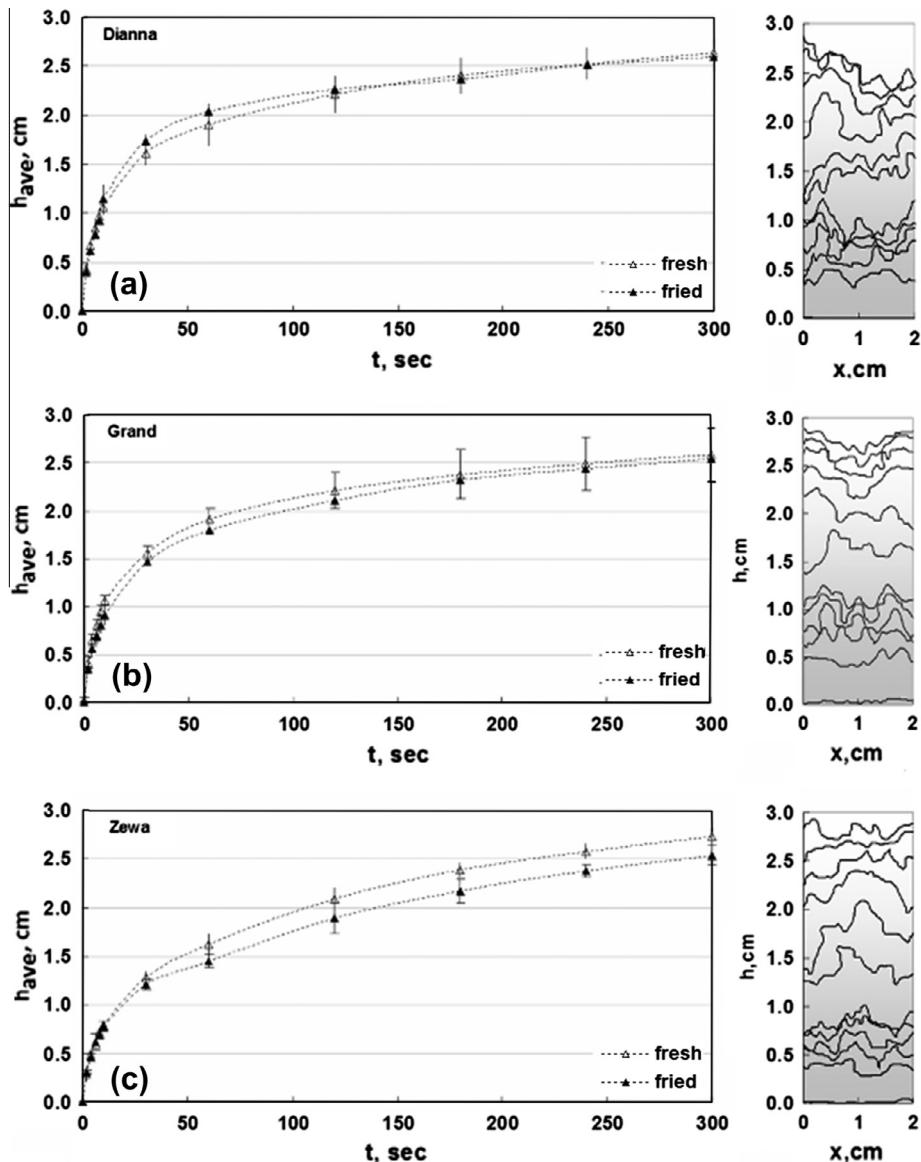


Fig. 3. Wicking front propagation at $T = 30^\circ\text{C}$, for fresh and prolonged fried oil into three different papers: (a) Diana, (b) Grand, and (c) Zewa. Inset at right hand side: wicking fronts for fresh oil at progressing time intervals. All three papers are commercial household double-ply paper towels.

Mediterranean countries (Kalogianni et al., 2010). A comprehensive list of the most important advantages of frying food with olive oil can be found elsewhere (Bastida and Sanchez-Muniz, 2001). The polar compounds of the fresh and fried oil have been determined with the microscale column chromatography method as 0.2% and 18.9% by mass, respectively (Nystazou, 2011). Thus, olive oil even after 40 frying batches has polar compounds below the rejection limit of 25% claimed by international laws.

Dynamic shear viscosity measurements are conducted with a MCR 301, TruGap®, Anton Paar cone-plate rheometer (CP50-1/TG, cone angle: 0.982° , plate diameter: 49.964 mm, truncation: $49.0 \mu\text{m}$; volume of oil used for viscosity measurements 0.57 ml). Details for the oil viscosity measurements can be found elsewhere (Lioumbas et al., 2012b). Surface tension measurements, γ , are conducted with a Wilhelmy plate tensiometer (TE2, LAUDA). The physical properties of the employed oils are presented in Table 1.

Two types of wicking papers are used. The first type refers to four household double-ply paper towels (brand names: Classic, Grand, Zewa and Diana). Double-ply towels combine the strong li-

quid retention capacity of two paper sheets with the strong capillary action of the void formed between the two sheets. The second type of wicking papers refers to single-ply chromatographic papers (Sartorius Chromatography Paper FT-2-526-254305N, FN30 and FN100 with nominal – as provided by the manufacturer – pore radius of 5 and $2.5 \mu\text{m}$, respectively). All papers are carefully cut in stripes 2 cm wide and 6 cm long. The microscopic structure of these papers is registered with a microscope (Axiostar Plus) equipped with a digital camera (Canon EOS-350D). Macroscopic (left) and microscopic (right) views of the papers used in this study are presented in Fig. 1. The macroscopic patterns pinched onto the household papers –usually as a means to fasten the two sheets– create appreciable heterogeneity along the stripes' width. Yet, at microscopic level all papers do not have uniform pores. As a matter of fact, the notion of a pore for a paper does not suggest a open channel inside a solid but a densely layered network of fibers, with the gaps between them forming an extremely irregular network of voids (Mc Donald, 2006; Koivu et al., 2009). Therefore, the aforementioned chromatographic papers nominal pores radius refers to a statistical average of voids.

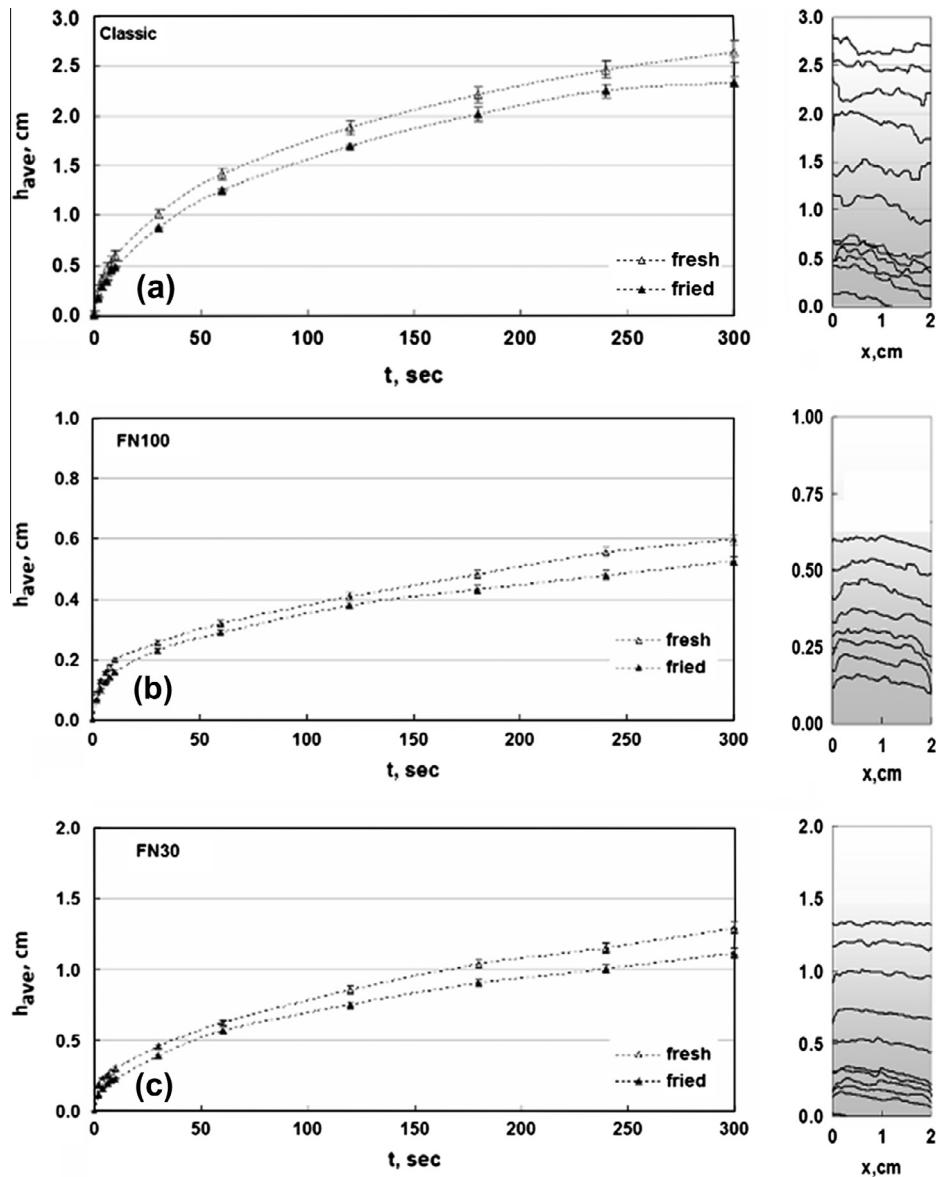


Fig. 4. Wicking front propagation at $T = 30^\circ\text{C}$, for fresh and prolonged fried oil into three different papers: (a) Classic, (b) FN100, and (c) FN30. Inset at right hand side: wicking fronts for fresh oil at progressing time intervals. Classic is a commercial double-ply paper towel; FN100 and FN30 are chromatographic papers.

2.3. Wicking experiments

Fig. 2a shows a schematic of the wicking setup. The up and down movement of the paper stripes is controlled by a laboratory jiffy-jack coupled with a cathetometer. A distance scale is marked on the stripes for ease identification of the wicking front during the experiments. The oil is contained within a transparent petri dish ($\varnothing 88 \text{ mm} \times 12 \text{ mm}$). In order to examine the effect of ambient temperature in the wicking performance, two different oil temperatures are tested (i.e. 20 ± 0.1 and $30 \pm 0.1^\circ\text{C}$). These represent low and high limiting operational (kitchen) temperatures common also in other frying oil rapid tests (VISCOPRIT, 2006). Paper stripes are kept at similar temperatures with the oil, by controlling the temperature of the surrounding air. The temperature of the oil in the Petri dish and along the height of the stripes is recorded with four K-thermocouples (accuracy $\pm 0.05^\circ\text{C}$) to assure temperature uniformity along the entire wicking path. It must be noted that the impact of evaporation of olive oil is negligible since it is practically not volatile at ambient temperatures.

A digital video camera (EUROCAM, desktop CCD, Cat No. VC 5000) is used to capture close-up images of oil penetration into paper stripes at 15 frames/s (image resolution 1024×760). The wicked area at every instant is manifested as a dark grey domain so that the oil front $h(t)$ is unambiguously determined (Fig. 2b). The instantaneous location of the front is processed by Image-Pro Plus software with an uncertainty of determining linear dimensions smaller than 1%. All experiments are repeated three times in order to check for reproducibility. The standard deviation of the wicking front measurements depends on the type of the examined paper as will be presented at next chapter. Synchronously with the above camera, a second camera (EUROCAM, desktop CCD, Cat No. VC 5000) furnished with a macro lens (Pentax, 50 mm f2.8) captures images of the papers thickness (image resolution 800×600) at 50 frames/s in order to investigate the swelling of paper fibers during the wicking tests (Fig. 2c). It must be stressed that the six wicking papers have different initial thickness. Preliminary experiments to compare the performance of the six wicking papers last 5 min. Further experiments to elucidate

wicking phenomena last 10 min which is still within the concept of a rapid test.

A wicking experiment starts by immersing a paper stripe to 1 mm below the surface of the oil in the Petri dish. This short immersion distance warrants that imperfections when cutting the stripe and loose fray fibers do not affect the onset of wicking.

3. Results and discussion

3.1. Wicking performance of the examined papers

Close-up images of the thickness of test papers (e.g., Fig. 2c) during wicking showed a smaller than 1.5% increase of paper thickness. This represents a very low degree of swelling contrary to what is observed when water is used as the wicking medium where swelling of the same papers reach up to 3% of the total papers thickness. Recently, (Masoodi et al., 2012), performed swelling measurements during absorption of several polar and nonpolar liquids to cellulose natural fibers and also observed that water yields an increased swelling effect compared to less polar liquids.

Figs. 3 and 4 present the wicking front propagation for all the examined papers for both fresh and fried oil at 30 °C. Wicking front patterns at specific time instants for fresh oil are displayed at the right hand side of each plot. Data points in these figures are instantaneous wicking front values, h , averaged over the width of paper stripes. The error bars at each data point stand for the standard deviation from three repetitions.

It is apparent that the *Diana* and *Grand* papers fail to discriminate between fresh and prolonged fried oil since the respective wicking front values are in close proximity. This is more so because of the substantial error bars in the data points. The failure may be partially attributed to the particular macroscopic patterns pinched on these papers. *Zewa* and *Classic* papers present a little better discrimination ability, but still error bars are appreciable because the instantaneous wicking fronts are too rough. It must be noted that all the above commercial papers have good oil penetration rates (i.e. ~5.0 mm/min) because of the double-ply structure offering a combination of small pores (within each ply) and large void (in-between plies). On the other hand, the chromatographic papers (Fig. 4b and c) have lower penetration rates (i.e. ~3.0 mm/min for FN30 and ~1.2 mm/min for FN100) but their wicking front is pretty flat when compared to the double-ply papers. This may be ascribed to their more uniform pore size distribution and their nearly flat (no pinched) surface. As can be seen in Fig. 4b and c, error bars in the data of the examined chromatographic papers are much smaller and do not overlap for most of the wicking period allowing **safe distinction** between fresh and fried oil. If this is so with the present fried oil having 18.9% polar compounds then it is reasonable to assume that the distinction will be better between fresh and even longer fried oil having 25% (or higher) polar compounds which represents the rejection criterion of fried oils. In other words, chromatographic papers can be considered as promising wicking media fulfilling the present study's objectives. Tests with several oil types fried at different durations (number of repeat batches) are underway to check the capacity of wicking tests over broader conditions.

In addition, the total amount of oil needed to perform a single wicking run is less than 1 ml (~0.15 ml wets the paper) which is below the quantities required by other viscosity related rapid tests. Apart from the above, we have made several attempts to pinch together two sheets of these chromatographic papers in order to make them behave as a double-ply paper offering higher penetration rates. However, these attempts have not been successful and so they are postponed to when more knowledge is acquired on the pinching process.

In summary, the specifications for a wicking rapid test are as follows:

- A paper should present **flat wicking fronts** during all stages of wicking. Deviations of the order of 1% along the width of the front are considered acceptable.
- A paper should allow distinctly **different wicking distances** between fresh and prolonged fried oil. Differences larger than 2–3 mm are considered adequate.
- A paper should provide appreciable wicking distance **in reasonable time**. Testing time up to 10 min is considered adequate.
- A paper should be **cheap, pretty stiff, easy to cut**. Chromatographic papers are a good option. Present results indicate it is worth manufacturing double-ply chromatographic papers for they might improve substantially the wicking performance.
- Higher oil temperatures** yield faster wicking and larger front propagation. Common kitchen temperatures are considered adequate.
- Wicking tests should be used in a **differential manner**. That is, instead of calibrating absolute wicking time (or wicking distance) against oils of known polar compounds, one needs only to compare the wicking time (or wicking distance)

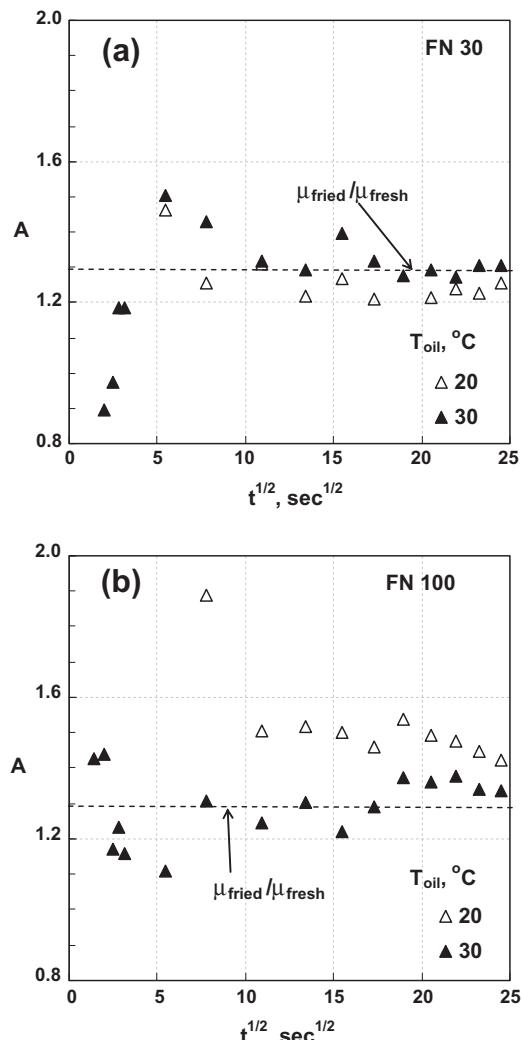


Fig. 5. Evolution of parameter, $A = (h_{fresh}/h_{fried})^2/(\gamma_{fresh}/\gamma_{fried})$, versus $t^{1/2}$ for chromatographic papers (a) FN30, and (b) FN100 at $T = 20$ and 30 °C.

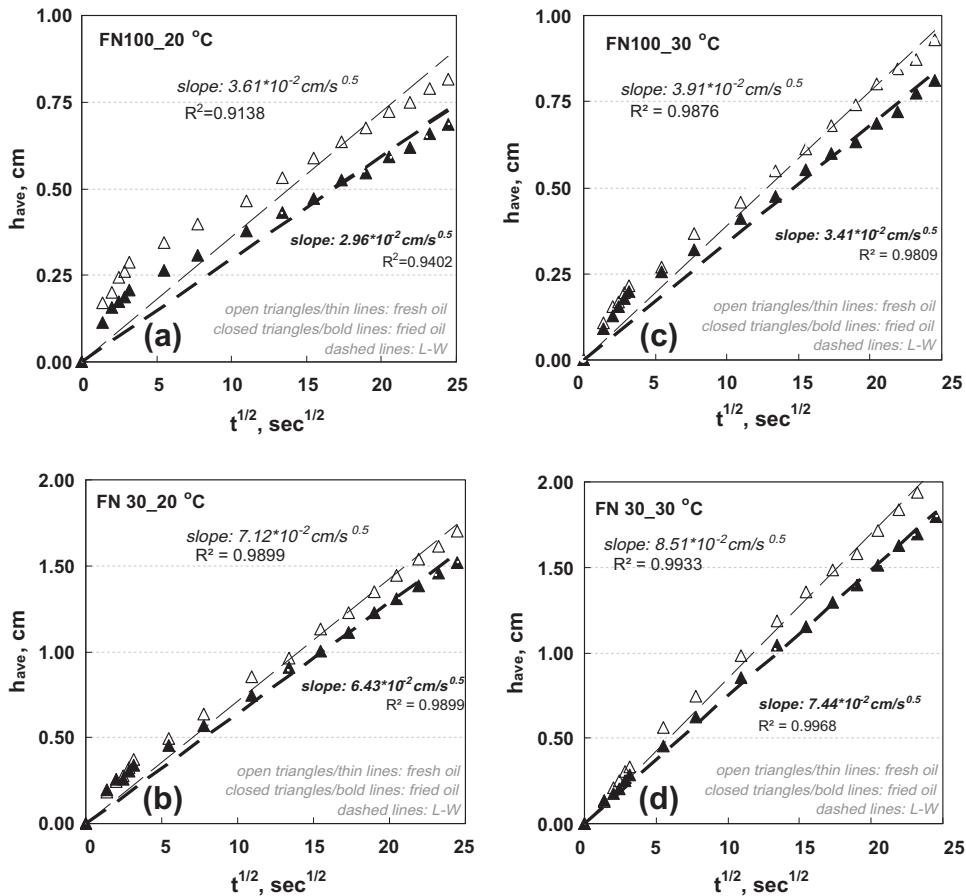


Fig. 6. Experimentally determined h_{ave} propagation (triangles) vs. L-W prediction (dashed lines) for the two chromatographic papers FN100 and FN30 and for both fresh and prolonged fried oil at $T = 20$ and 30 °C.

Table 2
Effective pores diameter, r_{eff} (μm) of the examined chromatographic papers predicted by fitting Eq. (1) to the present data (R^2 values in parentheses).

	Fresh oil		Prolonged fried oil	
	20 °C	30 °C	20 °C	30 °C
FN30 ($r_{nom} = 5.0 \mu\text{m}$)	2.79 (0.99)	3.03 (0.99)	2.68 (0.99)	2.72 (0.99)
FN100 ($r_{nom} = 2.5 \mu\text{m}$)	0.71 (0.91)	0.65 (0.98)	0.56 (0.94)	0.57 (0.98)

spanned by a fried oil to the wicking time (or wicking distance) spanned by the same fresh oil. This differential approach eliminates errors due to poor temperature control of oil samples which is common in catering and domestic applications.

3.2. Comparison with the Lucas–Washburn predictions

Comprehension of the physics behind wicking phenomena will allow design of porous media with particular characteristics that will better comply to rapid test requirements. As a first step to understand wicking of oil into paper we examine whether the wicking of oil into the employed chromatographic papers follow the well known Lucas–Washburn (L–W) equation, Eq. (1). This equation describes the penetration rate, $h(t)/t$, of a liquid that wicks a porous medium as a function of the geometrical properties of the porous matrix (i.e. effective pore radius, r_{eff}) and the physical properties of the fluid (i.e. viscosity, μ , surface tension, γ and contact angle, θ).

$$\frac{h(t)^2}{t} = \frac{\gamma}{2\mu} r_{eff} \cos \theta \quad (1)$$

The Lucas–Washburn equation is derived by combining the Poiseuille's law for viscous flow and the Young–Laplace equation for capillarity. The basic conditions for Eq. (1) to be valid are that laminar flow conditions prevail in the pores (Reynolds number must be below 1200) and that the formed liquid meniscus is roughly hemispherical (Fisher and Lark, 1979). The effective pore radius stands for the ratio of the average pore radius over a tortuosity factor (the latter is very difficult to determine). The Lucas–Washburn (L–W) equation has been frequently used in describing the liquid penetration kinetics inside thin layers of porous materials, despite the identified limitations (Schoelkopf et al., 2002):

If L–W holds in the present experiments, then (if paper pores size and oil contact angle remain constant), the square of the ratio of the wicking heights of fresh and fried oil, divided by the corresponding surface tension ratio, A , should be equal to the viscosity ratio of the fried oil over the fresh oil.

$$A = \frac{\left(\frac{h_{fresh}(t)}{h_{fried}(t)}\right)^2}{\frac{\gamma_{fresh}}{\gamma_{fried}}} = \frac{\mu_{fried}}{\mu_{fresh}} \quad (2)$$

In Fig. 5, the parameter A is plotted versus $t^{1/2}$ for FN30 and FN100 at $T = 20$ and 30 °C. In all plots henceforth data over 10 min of wicking are presented. The effect of surface tension is very small (i.e. 2.67% reduction between fresh and prolonged fried oil; Table 1) but it is taken into account. The decrease in interfacial

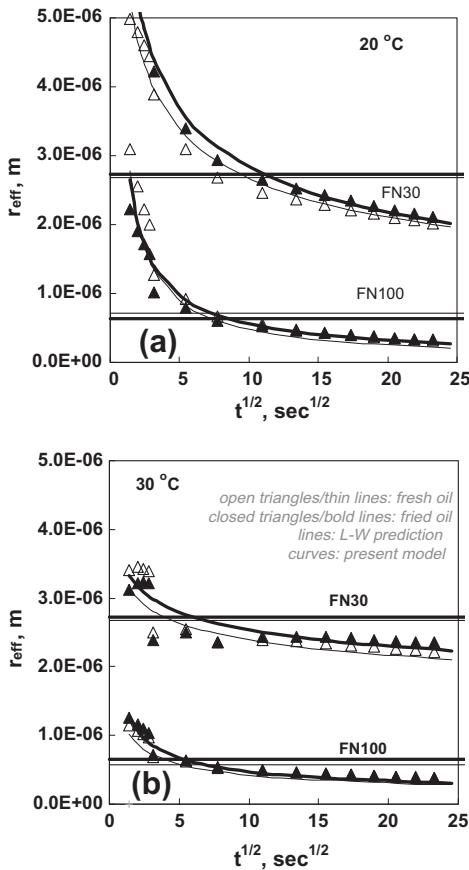


Fig. 7. Evolution of the instantaneous effective pore size, r_{eff} , (triangles) vs. the predictions of Eq. (4) (curved lines) and vs. the L-W predictions (Eq. (1); straight lines) for the two chromatographic papers FN100 and FN30 and for both fresh and prolonged fried oil at (a) $T = 20$, and (b) 30 °C.

tension that Kalogianni et al. (2011) and Valdes and Garcia (2006) reported, (3.36% and 2.13% respectively), for comparable frying parameters (i.e. frying duration, frying oil temperature and oil type), is quite similar to our findings (i.e. 2.67%). From Table 1 it is apparent that the analytically measured viscosity ratio between fresh and fried oil at 20 °C and 30 °C is alike, ~1.29. Other researchers also measured a significant viscosity increase for a wide variety of frying oils (e.g. Serjouie et al., 2010), measured a viscosity ratio 1.31 for palm olein and 1.40 for canola oil). Specifically, they fried slices of potatoes at 180 °C with a frying load of 1/35 kg_{potatoes}/L_{oil}, while each frying batch lasted 2.5 min (10 frying bathes per day with total frying time 17.5 h). Since during frying viscosity changes are about an order of magnitude higher than surface tension changes, wicking is dictated largely by viscosity.

In Fig. 5 it is seen that only for FN30, A agrees fairly with the analytically measured viscosity ratio for a large part of the wicking period. This looks better for the lower viscosity case, i.e. at 30 °C, although experimental fluctuations are comparable with those

for the higher viscosity case, i.e. at 20 °C. It is interesting that in all cases, A deviates from the analytically measured viscosity ratio more at the early stages of wicking and as wicking proceeds converges towards the expected ratio. This trend is more pronounced for the FN100 paper and for the lowest examined viscosity (i.e. at 20 °C). This is not surprising if one considers that during initial liquid penetration the flow pattern is complex and Poiseuille flow is not expected. As a matter of fact, we have noticed such discrepancies during wicking experiments of thin starch sheets (Kalogianni et al., 2004). These findings indicate that probably some of the commonly made assumptions for the derivation of the L-W equation are not valid for the conditions of the present study. In order to determine these conditions, a comparison of the experimental data with the L-W predictions follows.

3.3. Going beyond the Lucas–Washburn equation

Fig. 6 presents the wicking plots where the experimentally determined h_{ave} values (triangles) are displayed versus $t^{1/2}$ for both types of chromatographic papers (FN30, FN100), for both types of oil (fresh and fried olive oil) and for both examined temperatures (20 °C, 30 °C). The dashed lines in Fig. 6 represent the best fit of the experimental data with the L-W equation. The slope of these lines can be used to estimate the effective pores radius, r_{eff} , of each wicking medium inasmuch as viscosity and surface tension are known and contact angle can be taken as zero which is a common assumption for highly wettable materials. Estimated r_{eff} values are presented in Table 2. The deviation between the L-W predictions and the experimental data – by inspecting the R^2 values – is smaller at 30 °C (higher oil temperature) and for FN100 (smaller nominal and effective pores size) but it is alike between fresh and fried oil.

Since the pioneering work of (Washburn, 1921) many experimental studies have shown that Eq. (1) does not always predict satisfactorily the observed wicking patterns. A very common argument is about the term $r_{\text{eff}} \cos \theta$ in Eq. (1), which has been proposed not to remain constant **but be varying along the wicking process**. The latter has been attributed to different causes. For instance, to fibers swelling (mainly at works that involved wicking in deformable media e.g. (Masoodi and Pillai, 2010)), to only partial filling of the pores/cavities with liquid (at works that involve wicking over microstructured roughened surfaces, e.g. (Liu et al., 2011)), to the complex capillary flow through an interconnected pore structure with different pores sizes (Marmur and Cohen, 1997; Mehrabian et al., 2011) and to selective pore filling (Schoelkopf et al., 2002). An explanation has been suggested for a possible change of $\cos \theta$ related to the peculiar characteristics of the liquid flow field developed through axisymmetric capillaries (Marmur and Cohen, 1997). In our experiments we can rather neglect the effect of $\cos \theta$ because paper is inherently rough with high wettability so θ can be safely assumed as zero. In addition, we can rather exclude the small degree of swelling (>1.5% in cylindrical pore volume corresponds to >0.7% in pore radius at constant pore length) from the reasons justifying the failure of L-W to satisfactorily predict the experimental

Table 3

Dependence of $r'_{\text{eff}}/r_{\text{eff}}$ and b on oil viscosity and type of chromatographic paper.

Dynamic viscosity, μ (mPa s)	Fresh oil				Prolonged fried oil			
	20 °C		30 °C		20 °C		30 °C	
	$r'_{\text{eff}}/r_{\text{eff}}$	b	$r'_{\text{eff}}/r_{\text{eff}}$	b	$r'_{\text{eff}}/r_{\text{eff}}$	b	$r'_{\text{eff}}/r_{\text{eff}}$	b
FN30 ($r_{\text{nom}} = 5.0 \mu\text{m}$)	2.11	-0.17	1.10	-0.07	2.53	-0.19	1.26	-0.08
FN100 ($r_{\text{nom}} = 2.5 \mu\text{m}$)	5.63	-0.35	1.84	-0.23	6.25	-0.4	2.63	-0.25

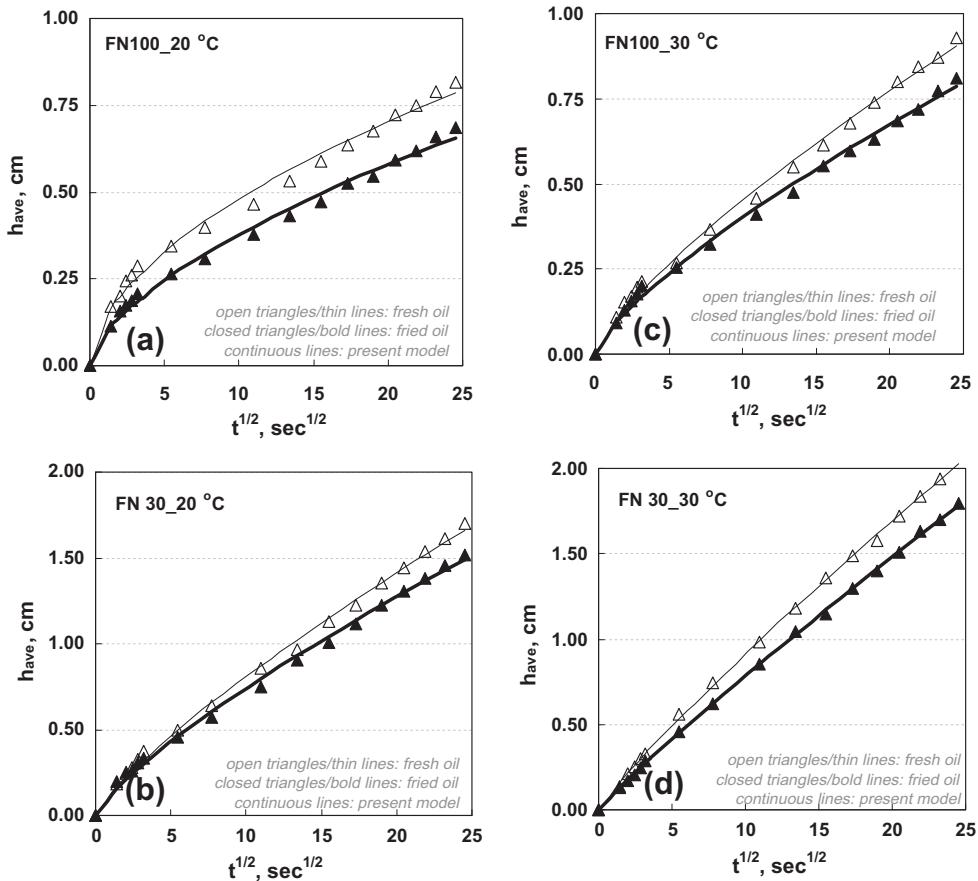


Fig. 8. Comparison between the experimental h_{ave} values and the model predictions for the two chromatographic papers FN100 and FN30 and for both fresh and prolonged fried oil at $T = 20$ and 30 °C.

data. Our attention is given next to the possible variation of the effective pores radius, r_{eff} , with time.

The most common approach (Masoodi and Pillai (2010); Masoodi et al., (2012)) to describe the evolution of r_{eff} during the wicking process, is to assume that it decreases linearly with time. Nevertheless, it is apparent (Fig. 7) that in our case, r_{eff} is not linearly decreasing with time but it follows rather a power law decay. The r_{eff} values presented as triangles in Fig. 7 are calculated from experimental data of h and dh/dt at distinct time intervals with the help of Eq. (3). The latter is a generalized differential precursor of the L-W equation when solving the appropriate force balance along the wicking front (Mullins and Braddock, 2012).

$$r_{eff}(t) = \frac{4\mu}{\gamma} h \frac{dh}{dt} \quad (3)$$

The continuous curves in Fig. 7 represent best-fit power law functions through the r_{eff} values:

$$r_{eff}(t) = r'_{eff} t^b \quad (4)$$

where r'_{eff} and b are empirical fitting parameters. Best fit values of r'_{eff} and b for all examined cases are displayed in Table 3. It is apparent that as the oil's viscosity decreases and pores size increases ($r_{FN30} > r_{FN100}$) then $r'_{eff} \rightarrow r_{eff}$ and $b \rightarrow 0$. (Cai and Yu, 2011) proposed a model where r'_{eff} depends from the tortuosity and the pore sizes, while b , is a function of the fractal dimension for tortuosity. The present experiments imply that oil wicking into paper might be an even more complicated problem, since r'_{eff} and b depend also on fluid properties.

Fig. 7 indicates that a power law function in Eq. (4) can describe fairly well the evolution of the instantaneous $r_{eff}(t)$. On the contrary, the constant r_{eff} values from Eq. (1) (straight lines) underestimates the pore size at the initial stages of wicking whereas overestimate it at the last stages of wicking. The magnitude of this deviation seems to depend both on chromatographic paper and on oil viscosity. Moreover, the $r_{eff}(t)$ profiles:

1. attain **higher** values at the early stages of wicking,
2. are **broader** (and **decrease faster**) at low oil temperature, and
3. converge to the same final value regardless of oil viscosity (due to test temperature or being fresh/fried); this value varies only with chromatographic paper.

Item 2 above is in line with the larger deviations from the original L-W found at 20 °C in Figs. 5 and 6. Furthermore, one would intuitively expect each chromatographic paper to have fixed initial $r_{eff}(0)$ which, however, later might vary differently during wicking at different conditions (temperature, fresh/fried). Yet, this is not what is found. Although the range of r_{eff} for each paper is alike, initial values are different and it is the final values at the end of wicking that appear to be fixed (item 3), independent from test temperature or using fresh/fried oil. A possible answer is that the discrepancy at the initial $r_{eff}(0)$ values is due to the complex flow pattern during initial liquid penetration that invalidates the L-W predictions. A more sophisticated approach has been suggested by Ridgway et al. (2002), who applied a 3D network pore model to simulate small and large capillaries filling. These authors argued about preferential filling of pores of different size depending on the

physical properties of the wicking fluid. So, in our case a possible physical picture might be that at the beginning of wicking, when all pores are vacant, larger pores fill first and this is more so for high oil viscosity (low oil temperature) where frictional pressure drop is greater at smaller pores. An even deeper understanding of the phenomena taking place during wicking should include pore randomness, kinetic roughening properties and fractal based theories for the understanding of the wicking front interface kinetics (Alava et al., 2004) but this is beyond the scope of this work.

Combining Eq. (3) with Eq. (4), the following expression is derived:

$$h(t)^2 = \frac{\gamma}{2(b+1)\mu} r'_{\text{eff}} t^{b+1} \quad (5)$$

Eq. (5) describes the wicking front propagation as a power law function and diminishes to L-W when $r'_{\text{eff}} \rightarrow r_{\text{eff}}$ and $b \rightarrow 0$. Fig. 8 compares the present experimental data with the predictions of Eq. (5). Apparently, there is a good agreement ($R^2 > 0.995$). It must be noted that several studies in the past (a recent survey is provided by Cai and Yu (2011)) described successfully the wicking front propagation with respect to time by power law functions different than the square root law of L-W. Here we make the hypothesis that the power law variation of wicking front propagation is attributed to a respective power law variation of the effective pore radius. This is in line with arguments regarding the gradual partial filling of the pores/cavities with liquid (Liu et al., 2011). Nevertheless, one should withhold judgment until further evidence is acquired to support this hypothesis.

4. Conclusions

This work provides experimental evidence that wicking of oil into paper can potentially be used as a new rapid test to **safely** and **easily** distinguish fresh from prolonged fried oil. The present wicking tests refer exclusively to fresh and prolonged fried extra virgin olive oil measured at two temperatures resembling ambient conditions throughout the year. Apparently, successful wicking tests with several oil types are required before a rapid test is established. Tests with different types of wicking papers demonstrated the role of the pore structure of the wicking medium in obtaining rapid and reliable measurements. Persistent deviations of the wicking profiles are observed from the well-known Lucas–Washburn behavior, but these deviations do not hinder the potential of test papers to be used as substrates for wicking rapid tests. A semi-empirical model has been proposed accounting for a decreasing effective pore size with time in the L-W equation. These model predictions describe well the present data and can prove helpful for the design of novel wicking media to be used as porous substrates for wicking rapid tests.

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