Combustion Characteristics of Candles Made from Hydrogenated Soybean Oil

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ABSTRACT: Hydrogenated soybean oil, referred to as soywax by candle makers, is a renewable and biodegradable alternative to paraffin wax in candle manufacturing. Soywax was investigated for its tendency to produce soot as well as potentially harmful organic volatiles (acrolein, formaldehyde, and acetaldehyde) during combustion. Beeswax and paraffin candles were used as references. A considerable amount of soot was produced from the combustion of paraffin candles, but little or none was observed from soywax candles. Compared to paraffin candles, soywax candles burned at a significantly slower rate and required less air. Small amounts of formaldehyde were detected and quantified in the fumes of burning paraffin candles. However, formaldehyde peaks found in the chromatograms of soy- and beeswax candles were similar to or slightly higher than that of the blank. Since soywax candles exhibited burning properties similar to those of beeswax candles, soywax shows promise in candle applications.

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KEY WORDS: Candle, combustion, hydrogenated oil, organic volatiles, soot, soybean oil, soywax.

For years, petroleum-based paraffin wax has been used as the main component of candles. Volatile organic compounds and small particles, commonly referred to as soot, are either directly emitted from the source material during combustion or produced as a result of incomplete combustion of paraffin wax (1,2). The soiling of interior surfaces of buildings due to soot deposition was reported by Fine *et al.* (2). The binding of soot to delicate materials, such as fine art, is a major concern since it darkens surfaces of valuable artifacts such as paintings and sculptures.

Soywax is a potential paraffin substitute that is biodegradable, renewable, and environmentally friendly. However, its burning characteristics are not well known. Lau *et al.* (1) reported that 27 ng/m^3 acrolein was produced from the combustion of 540 g stearin (a glycerol-based wax) for 3 h in a 40-m^3 room. Soywax is also a glycerol-based material. Acrolein is believed to be toxic to humans and animals (3), and at 0.13 mg/m^3 level, it can irritate the eyes upon exposure for 5 min. At 0.7 mg/m^3, it can affect the respiratory tract. The objectives of this work were to investigate the combustion properties of soywax and compare them with those of paraffin and beeswax candles.

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EXPERIMENTAL PROCEDURES

Materials. Naphthalene (laboratory grade, internal standard) and formaldehyde solution (37%, external standard) were purchased from Fisher Scientific (Fair Lawn, NJ). Acrolein (90%) and acetaldehyde used as external standards were obtained from Eastman Kodak Co. (Rochester, NY). 2,4,6-Trichlorophenylhydrazine (TCPH) (99%) was from Sigma-Aldrich Inc. (Milwaukee, WI), and carbon disulfide (CS_2) was from Matheson Coleman & Bell (East Rutherford, NJ). Soft paraffin with a broad melting range (25–80°C) and hard paraffin with two melting peaks at 32 (minor) and 49°C (major) were obtained from Dussek Campbell (Skokie, IL). Soywax (14.5% palmitic acid, 34.1% stearic acid, and 51.4% oleic acid, calculated iodine value: 46) was purchased from Cargill Co. (Minneapolis, MN), and beeswax from Strahl & Pitsch, Inc. (West Babylon, NY). Air (medical grade, USP) used for in-chamber combustion of waxes was obtained from Praxair Inc. (Danbury, CT).

Candle preparation. Approximately 200 g of wax was used to prepare each candle. Each one (soywax, beeswax, or paraffin) was melted and poured into a glass container (7.0 cm in diameter) with a wick (made of a cotton strip with a metal disk connected to one end) held in the center. To avoid cracking, chipping, and/or deforming of the candles during cooldown, wax was poured in several steps, allowing the waxes to solidify between steps. Soywax and beeswax were used without any additional manipulation, but a 50:50 ratio of soft and hard paraffins (an appropriate ratio for proper melting; personal communication with industrial partner) was used for paraffin candles.

Melting and solidification behaviors. A differential scanning calorimeter (DSC) model DSC 6200 (Seiko Instruments Inc., Chiba, Japan) equipped with a cooling controller using liquid nitrogen and an Exstar 6000 communication device (Seiko Instruments Inc.) was used to evaluate the melting and solidification behaviors of the waxes. AOCS recommended practice Cj 1-94 (4) with modification was used to program the DSC system. An initial hold for 2 min at 30°C followed by ramping at 30°C/min to 80°C and holding for 10 min was applied. Then, a cooling step at 10°C/min to −40°C and 1-min hold followed by a heating step to 80°C at 10°C/min were used.

Soot determination. For the purpose of collecting soot, candles were placed on a loop standing at a height of 49.5 cm above the benchtop. Initially, a funnel (15.0 cm in diameter) that was equipped with a membrane filter and connected to a vacuum pump was positioned upside-down (Fig. 1A) away

from the candle. To collect soot, the funnel was moved next to the burning candle so that the lip of the funnel was 29 mm below the edge of the candle container. Membrane filters with 5-µm pore size (SKC Inc., Eighty Four, PA) were used to collect the soot. Since flame disturbance can happen at typical room conditions, soot collection was performed under both disturbed and undisturbed burning conditions. Disturbance was defined as the small turbulence occurring on the flame due to air draft, which was implemented by using the lowest speed of a model 3733 Lasco fan (Lasco Products, Inc., West Chester, PA). The fan was located 112 cm away from the candle stand. Between two successive collections, the candle was allowed to continue burning but the fan was turned off. Normal room conditions were considered as nondisturbed or undisturbed conditions. Air velocity at the tip of the candle flame during the disturbed condition was 0.71–0.77 m/s as measured by a model 8455-12 air-velocity transducer (TSI, Inc., St. Paul, MN).

A Hunter colorimeter (Hunter Associates Laboratory, Inc., Reston, VA) with a 1-in. (2.54 cm) aperture was used to measure the darkness of the membrane filters. The range of L value of the soot-coated filter is 0 to 100. The instrument was standardized by using a black tile for 0 and a white tile for 100 values.

Burn rate. To measure the candle burn rate under normal room conditions, three candles of each type were placed alternately on the benchtop (20 cm apart) and allowed to burn for 380 min. Overall burn rates were obtained by dividing the total weight loss during candle combustion by the total burn time. A second set of candles was used to measure dynamic burn rates wherein burn rates were measured at different intervals throughout the 5-h burning period. Pool diameters and flame sizes were measured several times during the combustion periods.

Collection and analysis of acrolein, formaldehyde, and acetaldehyde. To collect volatiles, burning was performed in a chamber (Fig. 1B) with an air flow rate of 3.5 L/min, below which paraffin flame could not remain lit and above which the

TCPH solution, used to collect aldehydes, was bubbled away. The fumes were allowed to pass through three consecutive impingers containing 30-, 10-, and 10-mL TCPH solutions (1.0 M phosphoric acid saturated with TCPH), respectively. TCPH precipitates aldehyde and ketone compounds as hydrazones (5). Collection was continued for 8 h, after which the TCPH solutions along with the precipitates from the three impingers were transferred to a separatory funnel. The precipitates remaining on the surfaces of the impingers were washed off (using 18–20 mL CS_2 as solvent) and added to the separatory funnel, where all of the hydrazone products were quantitatively extracted into the CS_2 phase, with vigorous shaking, and separated from the aqueous TCPH solution. As much as 97% of the total hydrazones is recovered with a one-step solvent–solvent extraction of carbonyl compounds as 2,4-dinitrophenylhydrazones into CS_2 (6). Therefore, a similar extraction level was assumed when using TCPH in this study, and only a single extraction into CS_2 was performed. Also, a blank extraction was performed using the same volumetric ratio of TCPH solution to CS_2 solvent as was used for the sample extraction (i.e., 50:18, respectively). All extracts in the CS_2 phase were stored under refrigeration until analysis.

A Hewlett-Packard series II model 5890 gas chromatograph equipped with an SPB-5 fused-silica column (30 m × 0.25 mm × 0.25 µm; Supelco, Bellefonte, PA) was used to analyze the CS_2 extracts. Both the injection port and detector (FID) were set at 250°C, and the oven temperature was programmed as follows: 5 min holding at 50°C, 10°C/min ramping to 230°C, and 22 min of final holding at 230°C.

Naphthalene, which had a retention time of 14.20 min, was used as an internal standard to normalize the peaks. A primary solution of internal standard was made by dissolving 30.0 mg naphthalene in 3.00 mL CS_2. Then, 200 µL of this solution was mixed with 1.00 mL of sample or blank solution, and 2–3 µL of the final solution was injected for GC analysis.

Formaldehyde, acetaldehyde, and acrolein were used as external standards for quantification purposes; these gave peaks at 20.13 (singlet), 21.17, and 21.70 (doublet) and 22.70 min (singlet), respectively. The doublet peaks in the case of acetaldehyde hydrazone were due to the production of *syn-* and *anti-*isomers specifically in CS_2 as solvent (6). Detection limits obtained in this study were 1.24, 0.96, and 0.76 ng for formaldehyde, acetaldehyde, and acrolein, respectively.

RESULTS AND DISCUSSION

Soot production. Preliminary experiments indicated a wide variation in the level of soot production when burning paraffin candles, in contrast to soywax and beeswax candles. Therefore, 10 paraffin candles were allowed to burn on a benchtop. A wide range of smoking behavior was observed in the early stages of burning. After about 1 h, all paraffin candles produced smoke with any air movement. Similar observations of 10 soywax candles did not detect any visible smoke.

Two consecutive 2-min collections (3 min apart) of soot were obtained from 7 of the 10 paraffin candles above, and
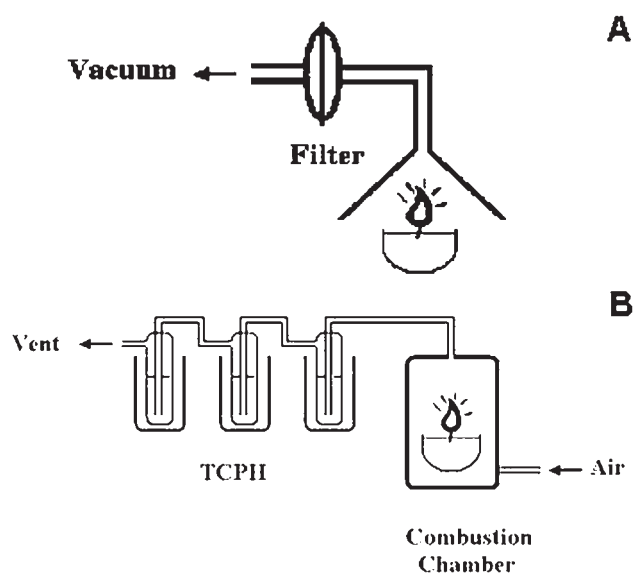

FIG. 1. Schematic of the apparatus used for the collection of soot (A) and aldehydes (B). TCPH: trichlorophenylhydrazine solution.

variations among all observations (i.e., 7 candles × 2 observations) were analyzed. There was considerable variation in the amount of soot produced among the seven candles (L values = 65 ± 34). This high variation in soot production was associated with the nonuniform structure of starting materials (i.e., the soft and hard paraffin waxes) as well as possible variations in the crystallization during the solidification of different candle batches. For soywax and beeswax candles, the consecutive 10-min collections indicated that the total soot produced over each collection period was negligible (hardly visible), for which colorimetric L-values of 90 or better were obtained.

For paraffin, seven separate collections (2 min per collection over 62 min of burning) were performed under disturbed conditions from two of the soot-producing candles identified above, for which a mean colorimetric L-value as low as 18.7 was obtained. The average L-value was 32.4 ± 14.4 (mean ± SD). This L-value was far below those obtained for soywax and beeswax candles under similar conditions (95.0 ± 0.4 and 94.4 ± 2.3, respectively). In a separate experiment, one candle from each type was selected and soot collection from the disturbed conditions was compared with that of nondisturbed conditions (Fig. 2). Average colorimetric L-values of 11.6 ± 0.8, 95.0 ± 0.9, and 86.7 ± 0.1 were obtained for two successive collections of disturbed paraffin (2-min collections), soywax (10-min collections), and beeswax (10-min collections) candles, respectively (Fig. 2). The 10-min collections for soy-

and beeswax candles were due to the fact that no soot was collected within the 2-min periods applied to these types of candles. For the 2-min soot collections from nondisturbed paraffin candles, an average L-value of 83.6 ± 1.1 was obtained, indicating a major effect from the disturbance in airflow. For the 10-min collections from nondisturbed soywax and beeswax candles, average L-values of 95.8 ± 0.0 and 95.7 ± 0.7, respectively, were obtained. During candle combustion under typical conditions in many places, flame disturbance by walking individuals is inevitable, and therefore paraffin candles will produce soot.

The results from the experiments above are for unscented paraffin candles. A higher amount of soot was reported by Krause (7) when scented paraffin candles were burned. Likewise, limited quantities of soot can possibly be produced with scented soywax candles depending on source and quantity of the materials added for such purposes.

Wax consumption rate. For in-chamber burning of candles (when collecting volatiles) at a 3.5 L/min air flow, burning rates of 3.21 ± 0.37 and 4.26 ± 0.24 g/h were obtained for soywax and paraffin candles, respectively. The air demand for burning paraffin candles under controlled air flow was much higher than that of soywax candles. Paraffin candles were extinguished if the air flow fell below 3.5 L/min.

Wax consumption rate was also determined when candles were burned outside the chamber at ambient conditions. Six soywax, three beeswax, and three paraffin candles were burned simultaneously for 380 min, and burning rate and pool diameter from each candle were measured (Table 1). Three of the soywax candles were trimmed as necessary. Untrimmed soywax candles burned at somewhat lower rates than paraffin candles (4.50 ± 0.22 vs. 5.08 ± 0.18 g/h), whereas the trimmed soywax candles had much lower burn rates (3.89 ± 0.28 g/h). This correlated well with the flame size (Fig. 3) of soywax candles, which was smaller than that of paraffin candles. Reduced wax consumption rate extends the burning time considerably for a given candle size. A smaller flame also can be associated with lower heat production suggesting that for some indoor applications where heat of combustion is an issue soywax candles have advantages. Under ambient conditions these observed burning rates were higher than those for candles burned in a chamber under controlled air flow.

The differences in the chemical compositions of soywax and paraffin contribute to their different combustion behaviors. Whereas soywax is a TAG, paraffin is a petroleum-based
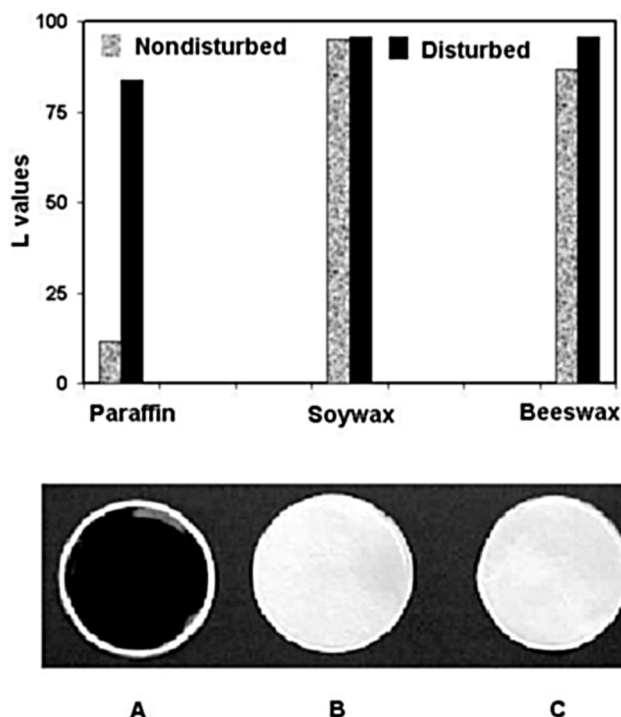

FIG. 2. Top: Colorimetric data as indicators of soot production for different types of candles under different air movement conditions. Results for paraffin are for 2-min and those for soywax and beeswax are for 10-min collections. Bottom: Typical images from the soot collected during the disturbed combustion of the waxes: (A) paraffin (2 min), (B) soywax (10 min), and (C) beeswax (10 min) candles. The longer times for soywax and beeswax collections were due to the lack of any soot at 2-min collections.

TABLE 1
Combustion Properties of Three Different Types of Candles over a 380-min Burning Period

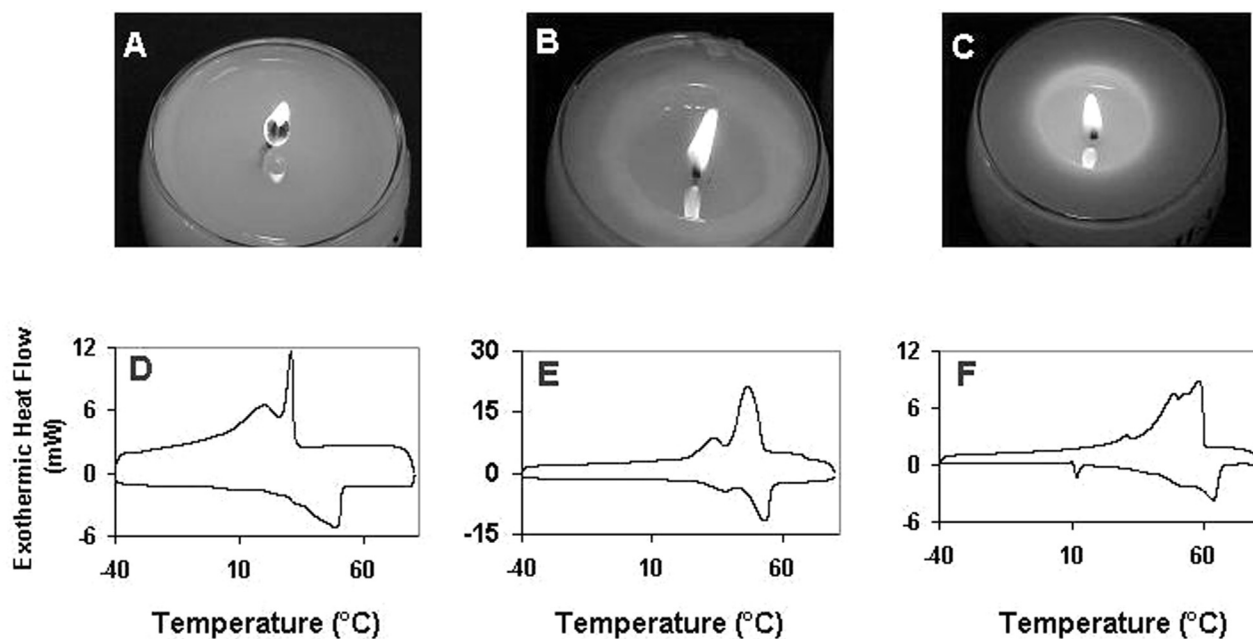| Candle type	Burning rate[a] (g/h)	Pool diameter[a] (cm)
Soywax (trimmed)	3.89 ± 0.28	5.4 ± 0.2
Soywax (untrimmed)	4.50 ± 0.22	6.5 ± 0.4
Beeswax	3.28 ± 0.25	3.3 ± 0.2
Paraffin	5.08 ± 0.18	4.9 ± 0.5

[a]Mean ± SD (n = 3).

FIG. 3. Typical differences in liquid wax pool size and flame size among the three types of candles: (A) soywax, (B) paraffin, (C) beeswax. D, E, and F are the DSC thermograms of these waxes, respectively.

mixture of different organic compounds, 78% (w/w) of which are GC-extractable [i.e., the fraction of the derivatized sample that is extractable and elutable from the GTC column (2)] consisting of 93% (w/w) alkanes, 6% (w/w) alkanoic acids, and 1% (w/w) cyclohexylalkanes (2). Compared to paraffin, soywax contains larger molecules with lower volatility and less mobility through the wax. This results in reduced flow of the melted wax through the wick and therefore a lower consumption rate.

The burning rate of beeswax candles is also shown in Table 1. Among the different candles studied, beeswax candles burned at the lowest rate. Fine *et al.* (2) reported that 76% of the total unburned beeswax was GC-extractable organic compounds consisting of 67% (w/w) long-chain wax esters, 14% (w/w) alkanes, 15% (w/w) alkanoic acids, and 1% (w/w) alkenes.

Burning soywax candles resulted in a flower- or mushroom-like formation around the flame (Fig. 3A) as a result of wick deformation. Such formations, which were not observed with paraffin candles, could lead to a larger combustion area and thus higher wax consumption. Therefore, trimming was added to our protocol for evaluating the burning of soywax candles. For trimmed candles, the flower-like structures were broken or cut during the combustion period (380 min) every 45–60 min. The trimmed candles burned at a considerably lower rate than those not trimmed (Table 1). The reduced surface areas of the wicks with the trimmed candles resulted in smaller flames and therefore lower consumption rates. In reality, consumers do not need to perform a continuous trimming for cost concerns. However, to avoid potential fire hazards and to reduce soot production, manufacturers recommend trimming their candle products.

Burning rates under disturbed and nondisturbed conditions were also examined. The overall burning rate of soywax can-

dles under disturbed conditions for 2 h was 2.62 g/h. This was considerably lower than the burning rate obtained for soywax candles burning in normal room conditions (4.50 g/h). Similarly, paraffin candles under disturbed conditions burned at considerably lower rates than those burned under normal room conditions (3.85 vs. 5.08 g/h, respectively). For beeswax candles, there was no detectable difference between the burning rates of the candles burned under disturbed conditions and those burned under normal room conditions. However, slight changes in the burn rate were observed after the candles had burned under normal room conditions for a longer time.

Size of liquid wax (burning) pool. The diameter of the pool created by each type of candle was measured over the burning period of 380 min (Table 1). Soywax candles created wider liquid pools inside the walls of their glass containers than did paraffin candles (Figs. 3A and 3B, respectively). The liquid pools of beeswax candles were the smallest (Fig. 3C). Several parameters can influence the size of the molten pool. The melting and solidification profile of the waxes as obtained by a DSC thermograph (Figs. 3D, 3E, and 3F) plays a major role in determining the pool size. Melting onset and peak temperatures for soywax were lower than those of paraffin and beeswax, resulting in a more liquid wax during candle combustion. Another parameter in determining the pool diameter is the wick diameter. Paraffin and soywax candles with thicker wicks created larger pools and burned at higher rates. In container candles, the larger pool size may be desirable to clean the container walls as burning progresses, but too much liquid can drown the wick and extinguish the flame.

Dynamic combustion. The three types of candles were burned for 5 h in duplicate and the changes in weight were recorded intermittently (Fig. 4A). Paraffin candles had the highest combustion rates (Fig. 4B), which increased with time.
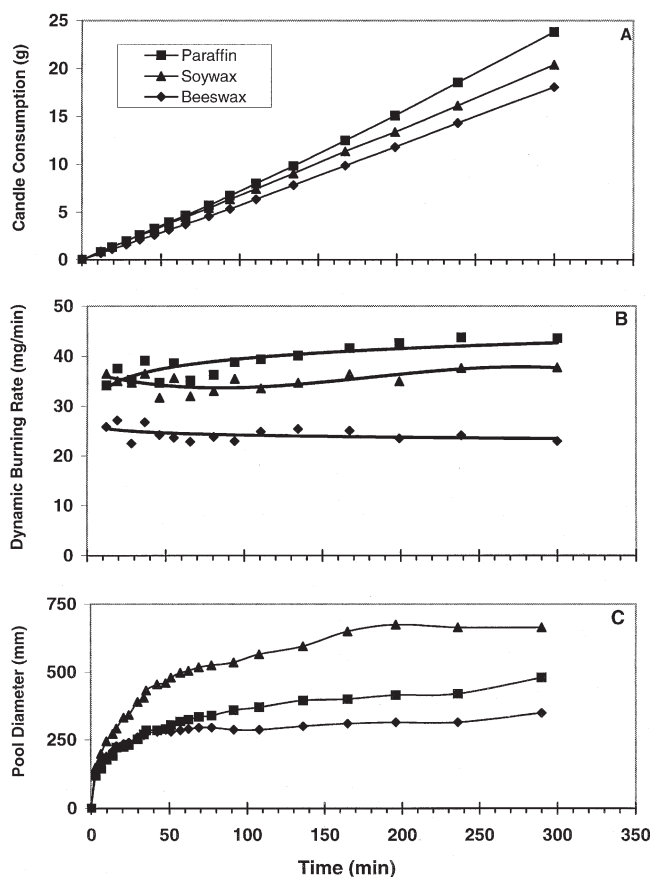
FIG. 4. (A) Profile of wax consumption in paraffin, soywax, and beeswax candles over time. (B) Dynamic combustion rate of paraffin, soywax, and beeswax candles. (C) Changes in the diameter of the liquid pool in the three different types of candles.

This was consistent with the higher soot production as burning continued. The combustion rates of soywax candles decreased within the first ~60 min but then slowly increased as burning continued. The decrease in combustion rate conformed to the decrease in soot production. Little or no changes were observed in the combustion rates of beeswax candles during the 5-h combustion period. The combustion rate of each candle type was consistent with the results from similar runs performed earlier.

The size of the liquid pool around the flame during the 5-h combustion period changed at a greater rate during the early stage of burning (0–40 min, Fig. 4C). The largest mean pool size was observed in soywax candles. The mean pool size of beeswax candles was initially similar to that of paraffin candles, but, as burning continued, paraffin preceded that of beeswax (Fig. 4C). Such behavior was consistent with the DSC melting and solidification behaviors discussed earlier.

The beeswax candles exhibited the most uniform flame shape, which was relatively small in height and width. After 2 h of burning, flame widths were 4.0, 5.0, and 6.0 mm for beeswax, soywax, and paraffin candles, respectively. The flame widths shifted to 6.0, 7.0, and 7.0 mm, respectively, after another hour of burning, when flame heights of 1.3–1.8, 2.0–2.6, and 3.2 cm were observed for beeswax, soywax, and paraffin candles, respectively. The flame shapes of the three different types of candles were quite different with paraffin candles being the largest and beeswax candles being the smallest. Untrimmed soywax candles were intermediate with a bulky flower- or mushroom-like formation in the center of the flame leading to uneven flames.

Characterization of combustion compounds. A typical chromatogram of TCPH-captured combustion products is shown
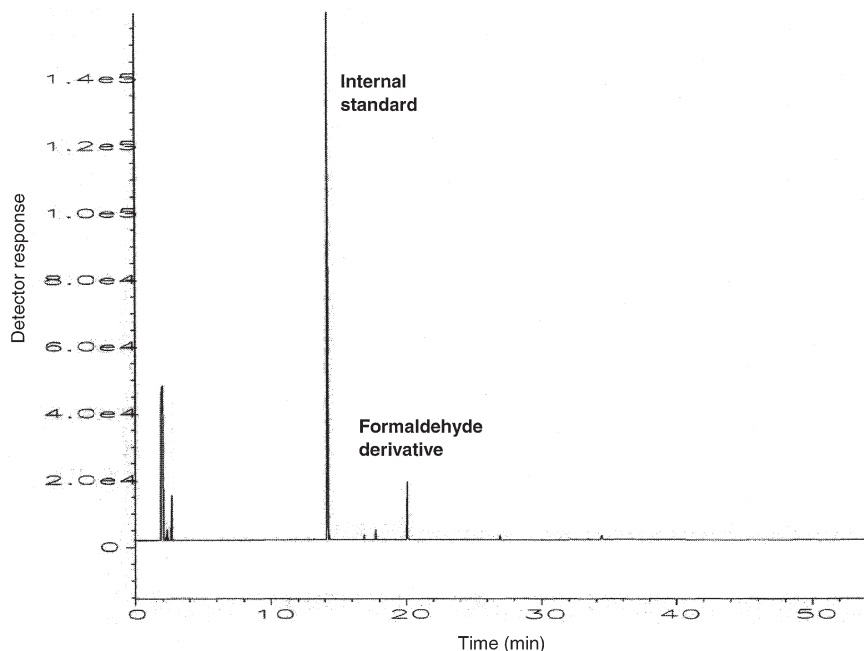

FIG. 5. Typical chromatogram for the trichlorophenylhydrazones of the fumes obtained from burning paraffin candles.

for paraffin candles in Figure 5. For soywax and beeswax candles, formaldehyde was detected at levels similar to or slightly higher than that of the blank, but its presence could not be confidently associated with the combustion of these waxes. A formaldehyde peak was obvious for paraffin candles, with an average of 1.7 mg formaldehyde per g combusted paraffin. Based on the minimum formaldehyde recovery of 54% in the system, as measured by a simulated run for a standard, a maximum of 3.2 mg formaldehyde is expected to be released for each gram paraffin consumed. No acrolein was detected in the combustion products of soywax, beeswax, or paraffin candles over a 5–8 h period. Lau *et al.* (1) reported that combustion of paraffin candles in a nondisturbed manner produced no volatile organic compounds that were of concern to human health.

Little information is available about health issues that may arise from the organic compounds emitted from paraffin candles. Lau *et al.* (1) quantified some of the materials collected and found that the levels emitted into a closed environment were far below their tolerance levels. Fine *et al.* (2) reported that many organic compounds were emitted during the combustion of paraffin candles. Their experimental procedure was not designed to collect lower-M.W. volatile organics, but many other compounds, such as alkanes and cycloalkanes, alkanoic acids, alkenes, and polycyclic aromatics, were found. Polycyclic aromatics are a health concern (8) and should not be present in a fully refined vegetable oil.

ACKNOWLEDGMENTS

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