Sulfur Compounds Affecting Processing of Rapeseed

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ABSTRACT

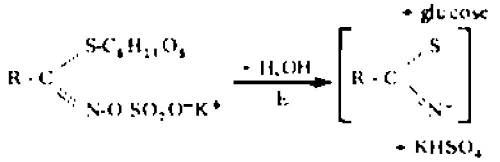
A characteristic feature of cruciferous oilseeds is a high level of sulfur compounds as sulfur containing amino acids and glucosinolates which determine the nutritional value of rapeseed meal and affect processing factors in oil mills. During rapeseed processing, products of glucosinolate splitting are liberated and attack metal and, as a result, a specific sulfur corrosion of oil mill equipment develops. The most exposed are cooker, toaster and transporters of wet meal. The results of industrial investigation of sulfur corrosion are described and the sensitivity to corrosion of several construction steels during rapeseed processing is considered. A high content of sulfur-containing compounds in starting oil significantly depressed the nickel catalyst activity and influenced the kinetics of rapeseed oil hydrogenation. Removal of these compounds by refining and its influence on the rate of oil hydrogenation are discussed.

INTRODUCTION

Processing cruciferous plant oilseeds, of which rapeseed is the typical representative, creates specific difficulties provoked by the occurrence of sulfur compounds in the seeds, mainly glucosinolates.

In this paper, we shall omit the problem of goitrogenic effects of glucoside derivatives present in rapeseed meal (RSM), which have already been thoroughly discussed by us (1,2) and other authors (3). We shall now pay special attention to the technological aspect of sulfur compounds as factors which make hydrogenation processes more difficult and favor corrosion of processing equipment.

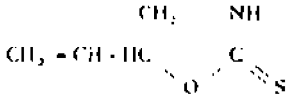
Sulfur compounds produced by hydrolysis of glucosinolates during processing of rapeseed are mainly isothiocyanates, thiocyanates and sulfates (Scheme I).



[I]

R-N=C=S	Isothiocyanate (ITC)
R-C≡N + S	Nitrile
R-S-C≡N	Thiocyanate
E	Thioglucoside glucohydrolase

The molecules of 2-hydroxy-3-butenyl-ITC cyclize spontaneously and rapidly (3) giving rise to oxazolidine-2-thione (OZT) (Scheme II):

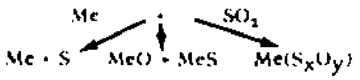


[II]

As a result of decomposition of these compounds, e.g., of isothiocyanates, hydrogen sulfide and several other sulfides are formed, which are especially active catalyst poisons (Scheme III).

$$\begin{aligned}&RNCS + H_2O \rightarrow R\text{-}NH_2 + COS\\&COS + H_2O \rightarrow H_2S + CO_2\\&2RNCS + 2H_2O \rightarrow 2R\text{-}NH_2 + CO_2 + CS_2\end{aligned}\qquad [\mathrm{III}]$$

Corrosion of metals in a medium containing sulfur oxides can lead to formation of oxides, sulfide and oxysulfide compounds (Scheme IV).



[IV]

These compounds are significant because production devices in oil mills processing rapeseed corrode more intensely than in oil mills that process other oilseeds, e.g., soybeans. Even a simple analysis by acidifying the scale from corroded equipment with hydrochloric acid shows the sulfuric character of the corrosion process (Scheme V).

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S \qquad [\mathrm{V}]$$

Corrosive changes of this type are favored by higher temperature, presence of steam and air, and acidity of the medium, which ranges from pH 4.8 to pH 6.8 in the processing of RSM (Rutkowski, unpublished data).

Through major decomposition of sulfuric substances present in rapeseed, sulfur can also occur in the atmosphere in such active forms as (Scheme VI):

$$\begin{aligned}&H_2S \text{ or } H_2S + H_2\\&SO_2 \text{ and } SO_2 + O_2\\&\text{fluid or gaseous S}\end{aligned}\qquad [\mathrm{VI}]$$

The corrosive action of hydrogen sulfide is especially important (Scheme VII).

$$Fe + H_2S \rightarrow FeS + 2H \qquad [\mathrm{VII}]$$

The corrosive power of iron sulfide is favored by the presence of oxygen, which transforms sulfides into oxides and releases molecular sulfur, which in turn reacts with hydrogen to form additional hydrogen sulfide (Scheme VIII).

$$FeS + O_2 \rightarrow FeO + S \qquad [\mathrm{VIII}]$$

Hydrogen sulfide dissolves in the acid medium of humid RSM to form a weakly dissociated solution (Scheme IX)

$$\begin{aligned}&H_2S \rightleftarrows H^+ + HS^-\\&HS^- \rightleftarrows H^+ + S^=\end{aligned}\qquad [\mathrm{IX}]$$

Hydrogen sulfide solution then reacts with iron, analogous to the electrolytic process (Scheme X):

$$Fe + S^= \rightarrow FeS + 2e \qquad [\mathrm{X}]$$

Details of the corrosive action of organic sulfur compounds present in RSM are unknown, although, according to Mrowec and Werber (4), activity of these compounds is much stronger than is attributable to the total content of sulfur in the medium. It can be presumed that the corrosion mechanism is analogous to the mechanism of hydrogen sulfide action.

The problem of poisoning of catalysts by sulfur has already been studied by several authors (5,6) but sulfur corrosion of equipment during processing of rapeseed was not thoroughly examined until now.

S-Compounds As Ni-Catalyst Poisons: Experimental Procedure

Rapeseed oil (RSO) used in this study was obtained from a continuous process industrial oil mill in Warsaw. The RSO (IV 102.1) used for hydrogenation was a refined bleached and deodorized oil (FFA—0.15%, PV 0.5 meq O_2/kg, P—0.6 mg %, S 0.5 ppm).

Sulfur content was determined according to Franzke et al. (6).

Allyl isothiocyanate (allyl-ITC) from the West German firm T. Schuchardt and 5-vinyloxazolidine-2-thione (OZT) of our own preparation were used for preparation of oil samples.

Hydrogenation was done in an open-type glass reactor with free hydrogen flow. Allyl-ITC and OZT were added to the hydrogenation reaction in amounts converted to sulfur in contents shown in Figure 1. Hydrogenation conditions were: weight of oil sample = 50 g; catalyst (Ni-formate) = 0.07% concentration; temperature = 180 ± 5 C; time = 60 min; hydrogen flow = 12 L H_2/hr atmospheric pressure (7).

RESULTS AND DISCUSSION

The majority of sulfuric compounds (95%) in processed rapeseed products remained in the RSM (8). Only a small fraction of sulfuric compounds initially present in rapeseed (less than 0.1% S) pass into crude oil.

During the process of degumming, glucosinolates can decompose to hydrogen sulfide, which can form water-soluble alkaline sulfides in subsequent refining. During the refining process, alkali-soluble OZT is removed to a great extent and allyl-ITC can decompose to CS_2 + CO_2 + $R-NH_2$, which can be easily removed during washing of oil (6). As a result, a considerable fraction of the sulfuric compounds is removed during the oil degumming and refining processes and the rest is removed in the form of volatile compounds during the oil deodorizing process (Table I).

Similar reduction of sulfur content in rapeseed oil processing has been found by Franzke et al. (6,9). Small quantities of sulfur, which remains in refined oil (4-22 ppm), however, can appreciably affect the poisoning of catalysts, decrease the number of usable catalyst alternatives, slow the rate of hydrogenation and increase consumption of catalysts.

Our earlier investigations (7,10) showed that, irrespective of the form in which sulfur occurs (allyl-ITC or OZT), its content, even in very low concentrations (less than 12 ppm), greatly reduces the Ni-catalyst's activity (expressed as the iodine value and melting point of fat, Fig. 1).

When refined oils are used for hydrogenation, complete removal of sulfur compounds is especially important. This was confirmed by hydrogenation of rapeseed oil which was repeatedly refined two and three times (Table II).

Increased growing of rapeseed varieties with low glucosinolate contents offers the possibility of reducing the difficulty in hydrogenation of rapeseed oil.

Corrosion: Experimental Procedure

Rapeseed used in industrial tests contained 44.1% oil. Processed meal contained 10.2 mg OZT and 5.3 mg allyl-ITC as aglucones per g.

The investigations were done in two oil mills (ca. 200 tons/day capacity). (a) oil mill A (basket-type extractor); (b) oil mill B (conveyer-type extractor).

Taking into consideration technical possibilities of equipment and staff observations, investigation locations were selected. The specification of these locations is presented in Table III.

A few kinds of construction steel were used for investigation (Table IV). The test specimens were prepared as standard plates (2 × 20 × 60 mm) with 6-mm hole diameter (Fig. 2) for hanging them on a special hanger. Before use, the test plates were cleaned with a wool cloth saturated with methanol or ether; then the plates were weighed (0.0001 g) and measured (0.1 mm). The corroded layer was removed by the use 5% HCl solution containing 0.5% of urotropin.

Corrosion measurements were conducted by determination of weight losses of test plates after the corrosion experiment. The results were expressed as: average corrosion velocity V_c and V_p; and average loss of weight of test plate (corrosion rate) G_c:

$$V_c = \frac{G_1 - G_2}{A \cdot t} \qquad \left[\frac{g}{m^2 \cdot 24\,h}\right]$$

$$V_p = \frac{365}{1000 \cdot d} \cdot V_c \qquad \left[\frac{mm}{year}\right]$$

$$G_c = \frac{G_1 - G_2}{G_1} \cdot 100 \qquad [\%],$$

where G_1 = weight of sample before corrosion test, g; G_2 = weight of sample after corrosion test, g; A = active area of sample before corrosion test, m^2; t = period of corrosion test, day (24 hr); and d = density of steel, g/cm^3.

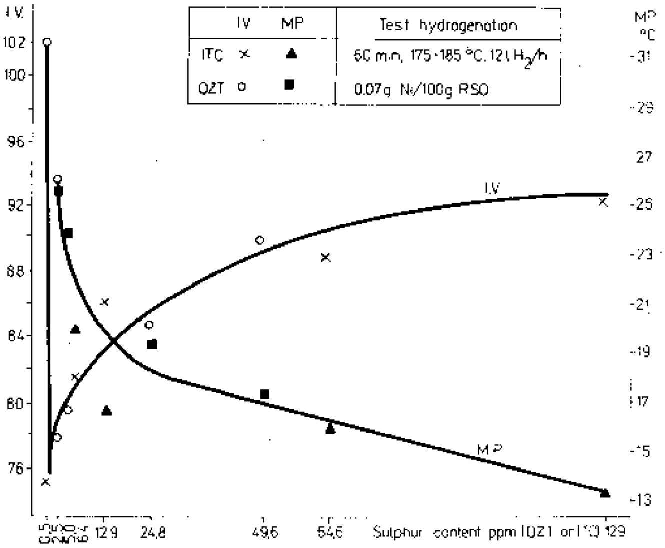


FIG. 1. Sulfur content (allyl-ITC and OZT) and reduction rate of Ni-catalyst activity by hydrogenation of oil.

TABLE I

Sulfur Content in Processed RSO

	(ppm)
RSO–crude	36
RSO–degummed	20
RSO–refined	12
RSO–bleached	10
RSO–deodorized	1

TABLE II

Sulfur Content and Hydrogenation Rate of Repeatedly Refined RSO

	S-content (ppm)	Hydrogenation rate (IV)[a]
RSO poorly refined	19	83.2
RSO twice-refined	6	79.1
RSO triple-refined	1	72.4

[a] IV reached under conditions given in Fig. 1.

TABLE III

Characterization of Investigation Locations

Investigation of location	Oil mill A	Oil mill B	Location of sample
Cooker		B1	Pipe carrying away vapors from cooker
Crusher of expeller cake	A2		Elevator of cake to crusher
		B3	Conveyor of crushed cake
Extractor	A4	B4	Chute scuttle of extractor
Toaster	A5		Pipe carrying away vapors from toaster
	A6	B6	Conveyor of freshly toasted RSM
	A7	B7	Pipe carrying away vapors from conveyor of toasted RSM

TABLE IV

Nominal Composition of Metals Used in Corrosion Tests

	Type of Polish steel				
	1H18NgT Ni-, Cr- Stainless	OH17T Cr- Stainless	10H Low Carbon	St3S Carbon	St3Sx
Corresp. AISI	316	430	—	—	—
Composition (maximum %)					
Ni	11.0	0.6	0.3	0.3	0.3
Cr	18.0	18.0	1.0	0.3	0.3
Mn	2.0	0.8	0.55	0.65	0.6
C	0.12	0.08	0.15	0.22	0.22
Ti	0.8	0.85	—	—	—
Si	1.2	0.8	0.6	0.3	0.07

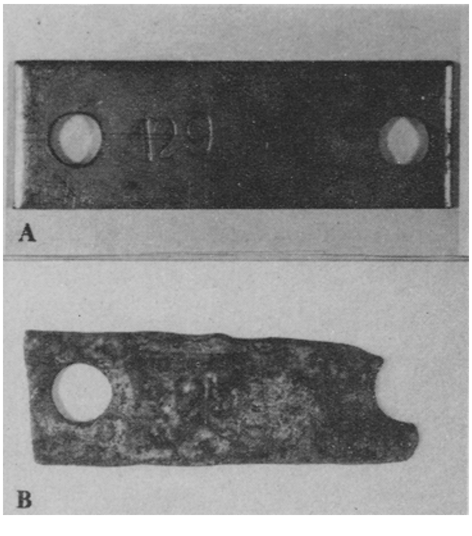


FIG. 2. Test plates after 4 months of corrosion experiment under toasting process. A = 1H18N9T; B = St3Sx steel.

RESULTS AND DISCUSSION

The rate of corrosion varies in consecutive stages of production. It is especially strong at the cooking, extraction and toasting stages (Fig. 3).

The results from the first investigation location (Table V)–a pipe carrying away vapors from the cooker–showed strong corrosive activity of vapors set free by cooking of crushed seeds. This results largely from liberation of free volatile sulfur compounds due to enzymatic hydrolysis of glucosinolates during the initial stage (up to 60 C) of heating to 85-90 C.

The samples that had been hung in conveyers of press cake (Table III) were characterized by small corrosion changes. The weight losses of carbon steel plates were only 0.4-2% during the 90 days of the experiment.

In the extractor (Table V), the corrosion was more active as the test plates were placed closer to the chute, where the atmospheric oxygen content is higher. This explains the relatively lower corrosion effect in the other parts of extractor.

Especially strong corrosion effects were found in the toaster (Table V). At this stage of the production process, many sulfur compounds in the form of ITC and its decomposition products are liberated. Additional factors favoring corrosion in this equipment include humidity and presence of atmospheric oxygen. The greatest corrosive activity in the toaster was found at conveyors of freshly toasted RSM and the vapor collector. Investigations of test plate surfaces have also shown intercrystalline and pitting corrosion, which is one of the most dangerous forms and causes quick and complete destruction of construction elements.

Comparisons of susceptibility of different kinds of construction steels to corrosion in the toaster (Table V, Fig. 2), have shown, without doubt, that the common steel (10H, St3S) is unsuitable for construction of rapeseed processing equipment, exhaust piping in cookers, some parts of extractors and toasters. Chromium-nickel or chromium steels should be used in these areas. Chromium steel has shown generally good resistance against corrosion,

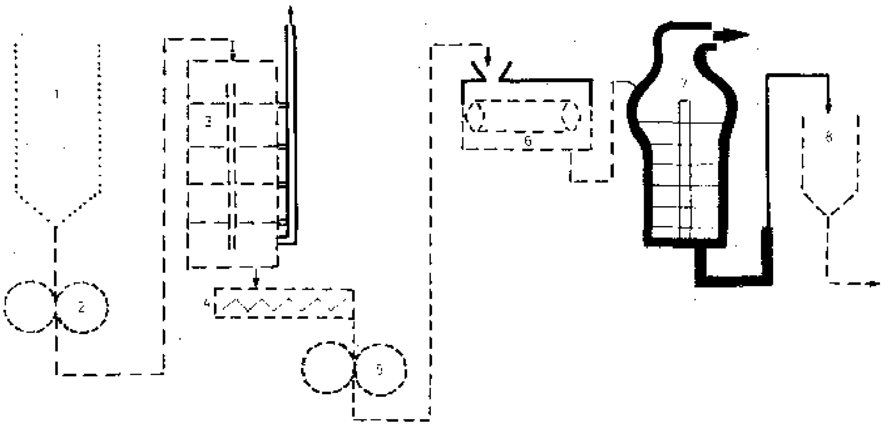


FIG. 3. General flow chart of rapeseed processing. Marked corrosion activity of rapeseed meal: · · · · lack; ----- small; ——— moderate; ——— strong. 1 = seeds silo, 2 = rolls, 3 = stack cooker, 4 = expeller, 5 = rolls, 6 = extractor, 7 = toaster-desolventizer, 8 = meal silo.

TABLE V

Comparison of Different Kinds of Steel on Corrosion Resistance during Industrial Processing of Rapeseed

Steel	Location of plate[a]	Duration (days)	Corrosion rate, G_c (%)	Duration (days)	Corrosion rate, G_c (%)
			Cooker		
10H	B1	134	23.4		
St3S	B1	134	43.0		
St3Sx	B1	134	32.2		
			Extractor		
10H	A4	149	11.2	238	14.9
St3Sx	A4	149	14.1	238	24.9
			Toaster		
OH17T[b]	A6	60	0	130	0.5
10H	A5	60	10.1	149	22.9
	A6	60	26.5	130	42.5
	B6	60	28.1	123	48.0
	B7	–	–	134	48.1
St3S	B6	60	42.6	123	64.1
	B7	–	–	134	68.8
St3Sx	A5	60	18.4	149	47.5
	A6	60	49.5	130	64.7
	B6	60	52.6	123	55.9
	B7	–	–	134	66.9

[a] According to Table III.

[b] The other specimens of 1H18N9T and OH17T did not show any corrosion changes at any investigation sites during the experiment.

TABLE VI

Corrosion Velocity of Carbon Steels during Rapeseed Meal Toasting Process

Steel	Location of plate[a]	Duration (days)	Corrosion velocity V_c $\left(\frac{g}{m^2\ 24\ hr}\right)$	Corrosion velocity V_p $\left(\frac{mm}{year}\right)$
	A5	60	17.0	0.85
		149	15.5	0.76
		238	12.5	0.63
10H	B6	60	32.7	1.63
		123	27.4	1.37
ST3S	B6	60	49.0	2.45
		123	36.6	1.83
	A5	60	20.1	1.00
		149	21.1	1.05
ST3Sx	B6	60	58.4	2.92
		123	31.1	1.56

[a] According to Table III.

but sometimes, still showed initial stages of pitting corrosion on the edges of test plates during the experiments.

The rate of metal corrosion changes with the passage of time (Table VI). In its first period, corrosion changes are rapid but with time, a layer of scale is formed on plate surfaces which reduces contact between the metal and the corrosive medium. The rate and character of the corrosion rate curve changes from parabolic to linear. Also, the scale causes considerable retardation of corrosive changes occurring in the processing of RSM.

The results of our investigations confirm the need for setting improved specifications for materials used to construct equipment for oil mills processing rapeseed. However, considering the different corrosive rates in individual rapeseed processing stages, materials can be selectively chosen so that equipment in less corrosive stages of rapeseed processing could be constructed from less resistant and less expensive types of steel.

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The Effect of Rapeseed Oil Added to Control Grain Dust on the Quality of Wheat[1]

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ABSTRACT

The effect of spraying edible rapeseed oil on controlling dust in barley, oat, rye and wheat has been investigated. Both the amount of rapeseed oil deposited and initial dust level govern the dust reduction level whereas the type of grain is immaterial. Regardless of the initial dust concentration, about 80% dust could be reduced with only 0.05% rapeseed oil addition. When the initial dust level exceeded 750 mg/m^3, dust reduction could reach 90%. Although some dust adhered to the wheat kernels after rapeseed oil application, except for slight deteriorations in flour ash and color, other flour analytical properties, physical dough properties, and milling and baking qualities were unaffected.

INTRODUCTION

Handling or processing grain creates dust. Aside from causing respiratory discomfort, dust particles of less than 5 μm in size are also considered a potential health hazard (1). In addition, grain dust explosions which have occurred in both grain elevators and flour mills are perhaps the most serious dust problem in the grain industry (2,3).

Controlling grain dust is very difficult because the dust becomes airborne whenever grain is moved or transferred. Furthermore, grain handling operations such as loading and unloading at a grain elevator are not usually confined to a small space. Effective grain dust control thus becomes extremely costly. Capital costs to install grain dust collection equipment have been estimated at between $250,000 and $1,000,000, depending on the size of the grain elevator. The annual operating costs are an additional one-fifth of the capital investment (4). Even after the grain dust is successfully collected (0.05-1.0% of the weight of the grain handled), unless it can find an end use such as becoming a feed or feed ingredient on the spot, it can create a solid waste disposal problem (4). There is an urgent need for new and improved dust control methods applicable to the grain industry.

Several methods have been used to control grain dust. Applying a continuous water mist via a series of fog nozzles in dusty areas has been suggested (5). Spraying extremely low levels of a hydrocarbon-base oil and soybean oil to wheat, corn and soybeans has resulted in surprisingly large reduction in grain dust levels (6,7). The aim of this study was to investigate the effectiveness of grain dust control by spraying the grain with an edible rapeseed oil and to study the effect of applying rapeseed oil on milling and baking qualities of Canadian Western red spring (CWRS) wheat.

MATERIALS AND METHODS

A grain dust measurement device was built according to Cocke et al. (6). A needle valve controlled the flow of air to exactly 1.5 L/min (measured by a Fisher Laboratory Flow Meter). Both the needle valve and the flow meter were installed between the cylinder containing the dirty grain and a vacuum pump. The vacuum pump was further connected to a Laboratory timer to control the dust sampling time. Grain sample size, sampling time and the procedure of measuring dust levels were the same as described by Cocke et al. (6) except that the dust collector contained a 47 mm, 5 μm Millipore membrane filter. Rapeseed oil was added to the samples by spraying directly into the rotating cylinder using a nitrogen-powdered atomizer.

Four dirty grains (barley, oats, rye and wheat) were used to study the effectiveness of grain dust control with rapeseed oil. The samples were obtained from rail car shipments and were subdivided and partially cleaned to provide subsamples with different dust levels. The rapeseed oil was slightly hydrogenated and was supplied by Canada Packers Limited Research Centre, Toronto. The fatty acid composition of the rapeseed oil was as follows: 16:0, 5%; 18:0, 3.4%; 18:1, 79.4%; 18:2, 8.9%; 18:3, 0%; 20:0, 0.6%; 20:1, 1.7%; 22:0, 0.3%; 22:1, 0.7%. For milling and baking studies, the wheat used was a composite sample of No. 1 CWRS type from the 1978 crop. The ash and protein (N × 5.7) contents were 1.51 and 13.4%, respectively (13.5% moisture basis). The wheat was mixed with 10% of a dust and chaff mixture obtained from the screen room of a local flour mill, to make dirty wheat.

Eight wheat samples were treated with various levels of rapeseed oil with or without 10% dust and chaff (Table I). After cleaning with a Carter Dockage Tester, they were tempered to 16.5% moisture for 18 hr and then milled in the modified Allis-Chalmers Laboratory mill (8). The amount of wheat milled was 3 kg based on 14% moisture to the first

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