Supercritical CO₂ Extraction of Lipid-Bearing Materials and Characterization of the Products

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ABSTRACT

Supercritical fluid extraction has recently become a reality in the petroleum, coal and food industries and is rapidly increasing in importance as its advantages become known. Advantages of carbon dioxide as a supercritical fluid include its low toxicity, low cost, lack of flammability, lack of reactivity, wide range of solvent properties at different pressures and temperatures, and improved properties of separated components in certain cases. Disadvantages of such extractions include high capital costs for batch extraction and lack of engineering hardware technology for continuous operation. In the supercritical CO₂ extraction of oil from soybeans, equilibrium solubility and high flow rates are readily achieved in a short-path batch reactor. The oil has a lighter color, less iron and ca. $\frac{1}{10}$ of the phosphorus contained in hexane-extracted oil. The lower phosphorus content results in lower refining losses. During extraction, some fractionation is observed to take place, with some more polar and/or higher molecular weight compounds having a tendency to increase in the later fractions. In a long cylindrical batch extractor, the flakes perform much like the stationary phase of a chromatographic column. The same advantages that result from extraction of soybeans also apply to the extraction of oil from cottonseed and corn germ. Cottonseed oil obtained by supercritical CO2 extraction has a lower gossypol content and requires less alkali for refining. In the extraction of wheat germ and bran, the oil has a lighter color, a milder odor and less unsaponifiables than that obtained by hexane. Free fatty acid contents were comparable, but tocopherol was higher in the supercritical CO, extract.

INTRODUCTION

Over one billion bushels (30 million tons) of soybeans are crushed each year for domestic use. Hexane has long been the preferred solvent for extracting the 6 million tons of oil from these beans. Recently, economic and social factors have revived interest in government and industry in searching for cheaper and safer solvents. Ethanol and isopropanol have been suggested; but ethanol is not an effective solvent at the concentration of its water azeotrope, and further rectification is costly. Isopropanol has a higher boiling point than ethanol and therefore is difficult to remove from both oil and flakes.

Supercritical fluid (SCF) technology may be a viable alternative to current extraction methods. The solvent

properties of SCF have been recognized for over 100 years but commercial applications have been slow in developing, possibly due to the sophisticated and expensive highpressure equipment and technology required. Although pressures to 3,000 atm are common in the chemical industry today, applications have usually concerned systems operated in a continuous manner. With the rapidly escalating costs and uncertain availability of petroleum solvents, and with the potential health and safety-related problems of both hydrocarbon and chlorinated hydrocarbon solvents, the social and economic environment has stirred renewed interest in SCF extraction. Supercritical carbon dioxide (SC-CO₂) is an ideal solvent because it is nontoxic, nonexplosive, cheap, readily available and easily removed from extracted products.

This paper reviews our experience with $SC-CO_2$ extraction of soybeans, cottonseed and corn germ and reports some new data for other oil-bearing materials.

EXPERIMENTAL

A flow diagram of the extraction apparatus is shown in Figure 1. One or more cylinders of commercial-grade CO_2 (A) are placed on a 1,000-lb capacity scale (B) with ¹/₂-oz sensitivity. The cylinders are wrapped with heating tapes controlled by an electric contact face on the cylinder pressure gauge (TP). Cylinder pressure is maintained at 1,200-1,250 psig, providing a nearly constant suction pressure for the compressor. The pressure gauge and cylinders are protected by a 1,500-psi rupture disc (RD-1). The gas passes through ¹/₈ in., 11,000 psi, 304 SS tubing and check valve (CV) to a 5- μ particulate filter (F-1), which protects the compressor diaphragms from scales and other foreign matter. The 10,000-psi double-end, air-driven compressor (C) delivers about 19 standard L/min at 8,000 psi with a suction pressure of 1,000 psig. The gas pressure is controlled by a variable (2,000-25,000 psig) back-pressure relief valve (RV). The temperature (TC-1) and regulated pressure (RP) of the gas are measured prior to entering the manifold leading to the extractor. The 2-L electrically



FIG. 1. Supercritical carbon dioxide extraction apparatus: (A) CO_2 cylinder, (B) balance, (TP) tank pressure, (RD1-3) rupture disc assemblies, (CV) check valve, (F1&2) gas filters, (C) diaphragm compressor, (RV) back pressure regulating valve, (RP) regulated gas pressure, (TC1-3) thermocouples, (SV1-6) shutoff valves, (AC1&2) gas coolers, (MV) micrometering valve, (FM) flow meter, (FT) flow totalizer and (EP) extractor pressure.

heated extractor $(2\frac{7}{16}$ in. id \times 29¹/₄ in. long) is a hydraulic cylinder made of 4340 steel with a working pressure of 15,000 psi at room temperature. The head, which contains a gas inlet, thermocouple (TC-2), rupture disc (RD-2) and glass wool particulate filter, is threaded into the cylinder and sealed with a standard O-ring closure. The compressed gas is then allowed to flow through the vertically mounted extractor in either direction by opening and closing the appropriate shutoff valves (SV-1, 2, 3 and 4). If the compressed gas temperature is above that required for the extraction (temperature varies with pressure), the gas is passed through an air cooler (AC-1 or 2) prior to entering the temperature-controlled extractor. The oil-laden gas leaves the extractor and passes through an electrically heated micrometering valve (MV) into a temperaturecontrolled, 1-L receiver. The receiver is slightly above atmospheric pressure, so the pressure drop across MV results in rapid cooling. Without applied heat, the extracted oil would freeze in MV and make flow control impossible.

The oil and gas phases separate in the receiver. The oil settles to the bottom and can be withdrawn as desired through SV-5. The CO_2 is passed through a filter (F-2) to remove entrained oil (<0.5% under all extraction conditions tried) and then through an instantaneous flow meter (FM) and a flow totalizer (FT) before being exhausted. Any pressure drop across the extractor is shown by a difference between regulated pressure (RP) and extractor pressure (EP). Likewise, any CO_2 leak in the system is indicated by a difference between the CO_2 weight loss measured at (B) and the total flow through the system (FT). A final rupture assembly (RD-3) is placed just ahead of the blowdown valve (SV-6) for the entire system. During the extraction, MV is adjusted until the desired flow (within compressor capacity) is indicated on the instantaneous flow meter (FM). The excess compressor capacity is then recycled through the backpressure valve.

Extractions were run on 0.2-2.4 kg quantities of oilbearing materials.

RESULTS AND DISCUSSION

Soybeans

Extraction at 5000-10,000 psig. The solubility of vegetable oil in SC-CO₂ varies with temperature and pressure (Fig. 2). For example, at 50 C the solubility increases with increasing pressure from <0.1% at 3000 psig to nearly 3.5% at 10,000 psig. However, above 8,000 psig a decelerating rate of increase is observed. Although one might expect a series of parallel solubility isotherms, the 50 C and 60 C isotherms cross at ca. 6,000 psig. This crossover of the solubility curves may be related to the densities of the SC-CO₂. Between its critical pressure (1,070 psig) and 6000 psig, CO_2 is quite compressible. The density, which is related to solute holding power, changes rapidly in this range; whereas above 6,000 psig the density does not change as rapidly. Therefore, the expected increase in solubility with increase in temperature would be observed at the higher pressures; but at the lower pressures, the increased solubility effect due to temperature may be overcome by the decrease in density and related decrease in solute holding power. Equilibrium solubility is readily established and maintained during the extraction of soybean flakes until nearly 90% of the oil has been extracted. Therefore, an increase in pressure from 5,000 to 8,000 psig significantly improves extraction efficiency at constant temperature (Fig. 3) (1), where extraction efficiency is defined in general terms as weight of oil extracted per unit weight of CO₂ passed through the substrate. On this basis, extraction efficiency should be maximized at the highest temperature that is consistent



FIG. 2. Effects of temperature and pressure on solubility of soybean oil in supercritical carbon dioxide. Data points on curves represent an average of 2 or 3 determinations.



FIG. 3. Effects of pressure on the extraction efficiency of soybean flakes at 50 C.

with product integrity, and at the highest practical pressure above ca. 6,000 psig.

Extraction above 10,000 psig. Another unusual and unexpected solvent characteristic of $SC-CO_2$ occurs at pressures above 10,000 psig. Contrary to previous predictions (2), at temperatures above 60 C the solubility of seed oils increases dramatically with increasing pressure above 10,000 psi (3-5). The apparent maximum solubility (>40%), as determined from extraction of the flakes or ground seed, is mass transfer controlled and varies with seed type, configuration and morphology. Below this apparent maximum, all extracted seed triglycerides exhibited the same equilibrium

solubilities under identical conditions of temperature and pressure. The rapid response of solubility to temperature and/or pressure allows much faster extraction rates and provides more economical methods of oil recovery. Because CO_2 is relatively incompressible at high pressure, recompression (pumping) costs are greatly reduced and the oil can be recovered by slightly reducing the pressure at constant temperature. Alternatively, reducing the temperature at constant pressure also affords good oil recovery.

An attempt to find an explanation for the unusual solvent properties of SC-CO₂ is being sought in solubility parameter calculations (6). The solubility parameter is of great practical value in predicting solubilities in systems at atmospheric pressure and room temperature. Through empirical expression, the estimation of these parameters allows extension of the concept to some supercritical fluids. The true solubility parameter is related to the internal pressure, which can be directly determined from pressure/ volume/temperature data. With a program written in Fortran IV and literature data, the internal pressure for SC-CO₂ has been computed at temperatures ranging from 40 to 100 C and for pressures up to 21,000 psi. Parameter values determined by use of these computed internal pressures (7) for SC-CO₂ are somewhat lower than those given by the usual empirical expression (8) computed from densities and critical pressures for corresponding conditions. It appears possible to compute solubility parameters for other supercritical fluids in the proper temperature and pressure range by slight modifications of the computer program.

Effect of other factors on extraction. Other potential factors affecting extractability include moisture, particle size and $SC-CO_2$ flow rate (9). Extractions of vegetable seeds with SC-CO₂ were run at constant temperature (50 C) and pressure (8,000 psig) while varying the moisture level and particle size. Soybean extractions were examined extensively; other seeds studied included peanuts and cottonseed. The rate of extraction and ultimate oil yields were quite low with cracked soybeans; however, good extraction rates and nearly theoretical oil yields were obtained from ground or thinly flaked (<0.010 in.) seeds. Moisture levels between 3 and 15% had little effect on extractability. Oil composition was not influenced by either parameter. Scanning electron microscopy was used to study seed structure before and after extraction with SC-CO2. At high flow rates the extractor dimensions (internal diameter [id] × internal length [il]) become an important factor. As the linear velocity increases for given id/il, a point is reached at which close packing of the substrate results in undesirable pressure drops. The ideal id/il must be determined based on the particle size, moisture and type of substrate being extracted.

TABLE I

Analyses	AOCS method ^a	Hexane	SC-CO ₂ b	
Yield	Ac 3-44	19.0	18.3	
Residual oil (%)	Ac 3-44	0.7	2.1	
Chromatographic refining loss (%)	Ca 9f-57	1.9	0.6	
Free fatty acid (%)	Ca 5a-40	0.6	0.3	
Peroxide value (meg/kg)	Cd 8-53	<0.1	< 0.1	
Unsaponifiables (%)	Ca 6a-40	0.6	0.7	
Fe (ppm)	Ca 15-75	1.45	0.3	
Phosphorus (ppm) ^c		505	45	

^aAOCS Official and Tentative Methods.

^bExtraction conditions: 50 C and 8000 psig.

^cPhosphorus determination by atomic absorption.

Oil properties. Exhaustive extraction of full-fat soybean flakes with SC-CO₂ yields an oil that is comparable to hexane-extracted oil, except for significantly lower iron and phosphorus contents. In a long cylindrical batch extractor, the flakes act much like the stationary phase of a chromatography column, which permits the recovery of lightcolored, essentially degummed, crude oil (Table I) (1,10).

The insolubility of phospholipids in SC-CO₂ is evidenced by the low phosphorus content of all oil fractions (Fig. 4). As expected, some fractionation takes place, with increasing concentrations of phosphorus appearing in the smaller final 2 fractions. The sparing solubility of phospholipids in SC-CO₂ is further substantiated (Table I) by the significantly lower chromatographic refining loss (0.6%) compared to hexane-extracted oil (1.9%). Therefore, the slightly lower oil yield (18.3%) and higher residual oil content of the flakes (2.1%) from SC-CO₂ extraction compared to hexane extracted oil contains ca. 1.5% phospholipids (1) based on the accepted calculation (percent phosphorus \times 31.7), whereas the SC-CO₂ extracted oil contains about 0.13% on the same basis. Likewise, the residual



FIG. 4. Phosphorus content of soybean oil fractions extracted with supercritical carbon dioxide at 8,000 psig and 50 C. Numbers in parentheses are the percentages of the total oil represented by each fraction.

oil from the SC-CO₂ extracted flakes is very high in phosphorus (2,500-3,000 ppm).

Fractionation is also observed with the unsaponifiables (Fig. 5); however, there is no significant difference in total unsaponifiables between SC-CO₂ and hexane-extracted oils (Table I).

Free fatty acids (FFA), because of their lower molecular weight, would be expected to concentrate in the earlier oil fractions. Although this is observed through the first 3 fractions (Fig. 6), the final 3 fractions show increases. These acids have not been isolated or identified. They constitute a very small percentage of the free acids in the oil and, based on their lower solubility in SC-CO₂, may have higher molecular weight or more functionality than typical FFA.

The iron content of commercially extracted hexane crude oil is significantly higher than $SC-CO_2$ -extracted crude oil (Table I). Like the phosphorus, the iron content of hexane oil is reduced to the same levels found in $SC-CO_2$ extracted oil by degumming and alkali refining (Table II).

The refined, bleached and deodorized (RBD) SC-CO₂extracted oil has good quality (Table III). The odor and flavor scores initially, and after 4 days' storage at 60 C, are not significantly different than the RBD oil obtained from degummed hexane crude oil. SC-CO₂ extraction, therefore, has the advantages of using a safe, readily available, low cost solvent; and, of eliminating a processing step (degumming) and its attendant oil losses without sacrificing the quality of the finished oil.



FIG. 5. Unsaponifiable content of soybean oil fractions extracted with supercritical carbon dioxide at 8,000 psig and 50 C. Numbers in parentheses are the percentages of the total oil represented by each fraction.

TABLE III



FIG. 6. Free fatty acid content of soybean oil extracted with supercritical carbon dioxide at 8,000 psig and 50 C. Numbers in parentheses are the percentages of the total oil represented by each fraction.

TABLE II

Effect of Oil Processing on Phosphorus^a and Iron Contents

	Hey	ane	sc-co ₂ b		
Processing step	Fe (ppm)	P (ppm)	Fe (ppm)	P (ppm)	
Crude	1.45	505	0,3	45	
Degummed	0.69	63	_c	_c	
Refined	0.11	28	0.07	35	
RBd	0.09	25	0.08	25	
RBD ^e	0.09	12	0.11	20	

^aPhosphorus determination was by atomic absorption. Values for refined, RB and RBD oils are near lower detection limits for AA method.

^bExtraction conditions: 50 C and 8000 psig.

^cDegumming not required for SC-CO₂ extracted oil.

dRefined and bleached.

eRefined, bleached and deodorized.

Meal properties. Soybean meal obtained by $SC-CO_2$ extraction, when toasted above 80 C and fed at 23% of the diet, produced growth rates in chicks not significantly different

Odor and Flavor Scores and Descriptions for Hexane- and SC-CO₂-Extracted Soybean Oil

		Odor			Flavor			
Descriptions		Hexane		SC-CO ₂ ^a	Hexane		SC-CO ₂ a	
	0-Time:	8.6	NSb	7.8	7.5(0.0) ^c	 NS	7.8(0.0) ^c	
Buttery		0.2		0.2	0.7		0.5	
•	4 davs.							
	60 Ć:	7.6	NSb	7,1	6.6(1.3) ^c	NS	6.0(1.7) ^c	
Buttery		0.6		0.9	0.6		0.9	
Beany		0.3		0.3	0.3		0.4	
Grassy		_			0.3		0.5	
Rancid		0.3		0,3	0.4		0.2	
Nutty		_			0.3			

^aExtraction conditions: 50 C and 8000 psig.

^bNo significant difference.

^cPeroxide values (meq/kg).

from those obtained with commercial feeds (11). The raw $SC-CO_2$ -extracted meal caused reduced growth, pancreatic hypertrophy and a change in digestive enzymes, as does the raw commercial product.

Corn Germ

The quality and storage characteristics of defatted germ flour obtained by SC-CO₂ extraction are superior to those of germ flours obtained by conventional hexane extraction (12,13). SC-CO₂ extraction efficiency for removal of triglycerides and bitter constituents (bound lipids) and for inactivation of peroxidase enzymes contributes to excellent initial flavor and storage stability of the germ flour. This highly dispersible protein flour has good potential as a balanced protein supplement in food formulations. Supercritical extraction of dry-milled corn germ yields a crude oil having a lower refining loss and lighter color than does oil obtained by expeller pressing. However, a distinct disadvantage of the process is that the crude oil obtained by SC-CO₂ extraction does not contain the native antioxidants normally found in crude expeller oil and therefore is much less stable to oxidation.

Proximate analyses of 4 extracted corn germ samples are given in Table IV. The effectiveness of the SC-CO₂ extraction was essentially the same for both the tempered and "as-is" germ. Only a small amount of triglycerides remained in these SC-CO₂-extracted flours, indicating excellent oil removal by extraction. In comparing these samples with laboratory prepared hexane-extracted germ flour, it was evident that SC-CO₂ is more effective than hexane both in reducing the total residual lipid level and in reducing the peroxidase activity. Reducing particle size of the germ by wet-grinding in hexane improves the extraction of lipid, but does not reduce the peroxidase activity.

Probably the most significant discovery in this application of SC-CO₂ extractions was the nearly 10-fold reduction in residual peroxidase activity of the germ flour. This heat-resistant oxidative enzyme normally is difficult to eliminate from food products even by toasting. The conditions used for SC-CO₂ extraction apparently denature peroxidase enzymes more effectively than do those used for hexane extraction. The mechanism of enzyme deactivation is not clear. This denaturation usually can be reflected in the reduction in nitrogen solubility index (NSI) of the untoasted SC-CO₂-extracted flours. Ca. 25% of the total nitrogen in germ flour is made up of free amino acids and peptides. The remaining nitrogen, comprised of high molecular weight proteins, was denatured as shown by the NSI value in Table IV. The reduction in peroxidase activity coupled with the low content of residual oil would indicate favorable control of oxidative rancidity during storage.

 $SC-CO_2$ -extracted corn germ flour with an initial flavor score of 5.8 (moderate flavor) showed little or no change in 5 weeks' storage at 37 C (5.8 score) or storage for two months at 29 C (6.0 score). As a frame of reference, allpurpose wheat flour has a score of 8.0 initially and after accelerated storage.

Cottonseed

Flaked cottonseed was extracted with SC-CO₂ at temperatures ranging from 50 to 80 C and pressures 8,000 to 15,000 psig (14). The crude oils were characterized for color, free fatty acid, total gossypol, phosphorus, refining loss and unsaponifiable matter and compared to hexane prepress and expeller produced commercial crude oils. Extraction of cottonseed with SC-CO₂ offers several advantages over conventional extraction methods, including lighter colored crude oil, less refining losses and lower caustic soda requirement for the refining operation. Preliminary data show that the gossypol content of SC-CO₂extracted crude oil is markedly lower than that of hexane prepress or expeller crudes.

Miscellaneous Oil-Bearing Materials

New data for SC-CO₂ extraction of a variety of oil-bearing materials are given in Table V. Pressures ranging from 8,000 to 11,000 psig and temperatures of 50-78 C resulted in essentially complete extraction of such materials as paprika, rice bran and wheat bran. Compositions of the resulting oils are shown in Table VI. Fatty acid contents are as expected. Noteworthy are the chlorophyl contents (as indicated by the green color) of avocado oil depending on extraction conditions used, and also the high tocopherol content of wheat germ oil.

The Future of Supercritical Carbon Dioxide Extraction

At present, supercritical extractions on a commercial scale are limited to decaffeination, production of a soluble hops extract and extraction of certain petroleum products. More

TABLE IV

Residual lipid Bound^c Peroxidasee Flours Triglycerideb Proteind Ash activity NSI lipid SC-CO2-extracted 8% Tempered germ 0.9 0.94 2.3 21.0 10.5 24 "As-is" germ 07 2.0 20.7 8.9 0.97 30 Hexane-extracted Liquid classified8 0.5 4.7 23.8 6.75 13.8 51 "As is" germh 8,7 7.28 2,0 20.9 11.2 58

Proximate Analyses of Corn Germ Flours Extracted by Hexane and SC-CO₂^a

^aExtraction conditions: 50 C and 8000 psig.

^bResidual triglyceride.

^cSoxhlet extraction, 20 hr hexane-ethanol azeotrope (82:18).

 d Kjeldahl, N \times 5.4.

eUnits/min/g germ.

^fNitrogen solubility index.

8Upper cut fraction obtained by classification. Sample was toasted, dry heat, 200 F, 20 min. hSoxhlet extracted, 5 hr.

TABLE V

Supercritical Carbon Dioxide Extraction of Miscellaneous Oil-Bearing Materials

Oil-bearing material	Pressure (psig)	Temperature (C)	Time (hr)	Moisture content (%)	Residual oil (%)	Oil recovered (g/100 g)	Oil description
Avocado (freeze-dried pulp)	11,000	70	24	3 4	5 3	58.2	Creen oila
Cottonseed	8,000	50	8	86	0.5	20.2	Light
Paprika	8,000	50	7	< 5	2.0	7 2	Viscous deem and
Peanuts	10,000	70-75	8	ě 0	0.9	49.0	Viscous, deep red
Peanut hearts	10,000	50	11	28	14	47.6	Light Off
Rice bran	9.500	70	6	63	0.9	10.2	
Sorghum bran	9,600	78	11	6.1	0.7	19.2	waxy
Sorghum germ	10.000	70	7	94	0.7	16.0	Waxy
Sovbean	8,000	50	8	11.4	0.2	10.0	Yellow off
Wheat bran	8,000	50	5	11.4	0.7	19.4	Light
Wheat germ	8,000	50	6	10.1	1.3	4.0 7.0	Waxy Light oil ^c

^aA green oil was produced at 10,000 psig and 80 C. Below 10,000 psig and 70 C, a yellow oil was obtained.

^bFlour was bitter.

^cBland odor. The oil contained 4.5% tocopherol.

TABLE VI

Composition of SC-CO₂-Extracted Oils from Miscellaneous Oil-Bearing Materials

Oil-bearing material	Fatty acid (GC area %)										_
	14:0	16:0	16:1	18:0	18:1	18:2	20:0	18:3	22:0	Unsaponifiables (%)	fatty acid (%)
Avocado	-	16.5	7.4	0.4	54.7	18.3		1 3		20	0.1
Cottonseeda	1.2	26.4	0.7	2.8	24.0	433	03	1.0		0.7	0.2
Paprika	7.0	14.4	_	3.6	13.2	50.9	10	8.8	_	0.7	1.5
Peanuts		10.7		2.6	57.6	29.6	1 1	1 1	10	-	- 0.1
Peanut hearts	-	16.9	_	1.9	38.4	36.9	10	1 9	2.0	1.2	0,1
Rice bran	0,3	18.0	0.3	1.2	40.0	38 3	-	22	2.7	5.0	0.2
Sorghum bran	_	12.7	0.6	1.8	32.0	50.2		27		3.0	13.5
Sorghum germ		12.8	0.4	1.0	323	514	_	1.0	_	-	23.1
Sovbean	0.1	113		38	23.6	53.6	_	7 2	_	2.0	5.0
Wheat germ			.4	no	data			<i></i>		4.6	0,2

^a0.4% Cyclopropenoid acids also present.

widespread applications including vegetable oil extractions will develop slowly as equipment used in the older processes wears out, and as the industry becomes more familiar with the sometimes surprising characteristics of supercritical fluids. Such characteristics are just now being discovered, and, no doubt, many more remain yet to be found as research progresses. Supercritical fluid extraction was recently described (15) as one of the "pacing technologies" in the fats and oils industry.

Surely one of the most important considerations in developing new extraction processes is the safety aspect. CO2 is nontoxic, nonexplosive and nonflammable, as well as being readily available at a low cost. The same cannot be said about hexane. About 2 years ago, an explosion ripped through the sewer system of Louisville, Kentucky, as the result of a leak from a hexane extraction plant. Sewer repairs amounted to 16 million dollars, street repairs were 1.5 million dollars, water line repairs were 0.7 million dollars and, on top of all that, a 250-million-dollar class action suit was filed against the company concerned (16). A new SC-CO₂ extraction plant would not even approach that total!

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