Filmed
1-8-79

Accession number 965

CONFIDENTIAL

Lorillard Research Center
Greensboro

INVESTIGATIONS INTO THE EXTRACTION OF NICOTINE FROM TOBACCO

Submitted by: J. R. Reid

Report number: ____________ Date: 2/7/77

Summary or Abstract:

Investigations have been carried out to find an inexpensive and efficient method of extracting nicotine from tobacco. A survey of the literature indicated that two promising techniques were the extraction with water or freon. Both procedures have been studied and result in an 80-85% reduction in leaf nicotine. The water method yielded directly a suitable smoking material but the nicotine recovery procedure involved elaborate processing. The freon-ammonia system afforded the nicotine in a straightforward manner but required further developmental work for the tobacco to be a suitable smoking material.

/lmh

Xc: Dr. H. J. Minnemeyer
Dr. R. S. Marmor
Dr. R. W. Slaven
Mr. R. L. Thomas
Library

CONFIDENTIAL

TABLE OF CONTENTS

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTIAL

LIST OF TABLES

CONFIDENTIAL

LIST OF DIAGRAMS

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTI

Lorillard currently desires to introduce a low "tar", moderate nicotine cigarette as a marketable sales brand. One means of accomplishing this goal is by the addition of nicotine, either as the pure alkaloid or as a salt at some point in the tobacco processing, onto a low tar, low nicotine blend of tobaccos.

The nicotine requirement for the yearly support of a sales brand of 10 billion cigarettes containing 600 mg of tobacco per cigarette and an added 1% nicotine amounts to 132,000 lbs/year.

Our primary objective was to study the economically feasible sources of nicotine and its isolation and recovery as the pure alkaloid or as a nicotine salt.

Previous estimates for the isolation of nicotine from our current stock of waste tobacco range from 40-45% of this total nicotine requirement depending upon which waste is utilized and specifically the efficiency of our recovery and isolation procedures.[1]

The remainder of the nicotine must be purchased as alkaloid, alkaloid salts or tobacco suitable for extraction. This tobacco must be processed and the nicotine subsequently isolated and recovered.

Since an isolation technique would be required, we began to study a variety of published procedures for the isolation of nicotine from tobacco.

The use of nicotine as a commercial insecticide has generated numerous methods for the extraction of nicotine from tobacco. All the methods for the extraction of nicotine can be broken down into four distinct categories:

1. Water Extraction.
2. Extraction with organic solvents with or without preliminary treatment of the tobacco.
3. Steam distillation directly from the tobacco.
4. Pyrolytic degredation of tobacco material and direct distillation of the nicotine.

These four areas were investigated for their relative advantages and disadvantages reported in the literature.

1. <u>Water Extraction</u>

The water extraction technique is one of the oldest methods used for the manufacture of insecticidal solutions.[2] This technique has been performed using either hot or cold water[3] or water which has been treated with alkali (ammonia, lime or lye).[4]

CONFIDENTIAL

The use of ultrasonication for the release of nicotine into the water has been shown to expedite the extraction process by rupturing "nicotine cells" within the tobacco matrix.[5]

A recent report[6] has indicated that green uncured tobacco can also be used. In an effort to reduce cost, a high nicotine tobacco (N. Rustica) was cut while green, water and lime were added and the juice expressed using sugar cane technology.

The solutions obtained by these water extraction methods usually contain 0.1% to 1.0% nicotine plus other dissolved or suspended tobacco material.

These extracts are then processed to concentrate the nicotine, either as the pure nicotine alkaloids or as a nicotine salt. The usual salt chosen has been the sulfate since aqueous solutions of this nicotine salt may be concentrated up to 40% before crystallization occurs upon storage. These 40% solutions are then marketed directly as insecticide under the name Black Leaf 40.

The reported methods for the concentration of nicotine from dilute aqueous solutions include high pressure steam distillation from alkalinized solutions[7] and organic solvent extraction.[8] The steam distillates then require an additional concentration step which has consisted of acidification followed by distillation or solvent extraction of realkalinized solutions. The large amount of organic solvent used to extract the dilute nicotine extracts must then be either removed by distillation to afford the nicotine alkaloids[9] or sequentially washed with aqueous acid solutions until the acid/nicotine concentration reaches the desired level.[9] The organic solvents used include kerosene,[10] methylene chloride, dichloroethylene, diethyl ether[11] and chlorobenzene[9]. The time required for an efficient extraction depends upon the favorability of the partition of nicotine between water and the organic solvent and the pH of the water or extracts[12]. [See Appendix]

2. Organic Solvent Extraction

Previous investigators have demonstrated that a variety of organic solvents can be used to extract nicotine from tobacco.

The tobacco can be extracted directly with methylene chloride[9] or methyl ethyl ketone[13] continuously to effect an excellent removal of the nicotine. The tobacco has also been treated with ammonia, lime or lye then extracted with other organic solvents, such as trichloroethylene, benzene, gasoline, kerosene, diethyl ether[10] or freon[14].

CONFIDENTIAL

In the case of the organic solvents immiscible with water, the extracts can be reextracted with aqueous sulfuric acid solutions until the desired concentration is reached. The organic solvents are recycled for further extraction. The methyl ethyl ketone extract was processed in a unique manner. The nicotine was reextracted from the organic solvent by the use of cold saturated aqueous salt solutions. The two phases were separated and then warmed, the salt phase was rendering the nicotine immiscible. The impure nicotine was separated as a distinct dark phase at the surface of these mixtures.[15] The organic solvents boiling lower than water also permitted direct fractional distillation to afford more concentrated solutions of nicotine since the heat requirement for concentration was substantially decreased.

3. Direct Tobacco Steam Distillation

The nicotine can also be extracted from the tobacco by direct steam distillation. With the exception of a small percentage of "free" nicotine, the majority of the nicotine in tobacco is bound as organic salts.[16] These salts have been neutralized by the use of lye or lime and the nicotine distilled from the tobacco directly by the use of steam. Again the distillate is a very dilute solution of nicotine in water and required further processing as described earlier.

The tobacco and stem material can be powdered to effect a more intimate contact between the alkali and the organic acids and thus free the nicotine[17] or alternately the alkali treated tobacco can be placed under a vacuum followed by a rapid release. This will rupture the nicotine cells, the nicotine from which is then steam distilled.[18] An alternate procedure was used in which a stream of ammonia was introduced continuously into a steam distillation apparatus.[19] The condensed distillate was then fractionally vacuum distilled to remove ammonia dissolved in the condensate.

4. Dry Distillation

The dry distillation technique has reportedly been used successfully on waste tobacco.[20] Tobacco material is treated with alkali and can be heated in a rotating drum with either vacuum or a slow heated air steam being passed through. The nicotine volatilizes and is passed into a series of condensing traps.[21] By this technique various tobacco wastes were processed for their nicotine content. All volatiles pass over and a purification step, usually vacuum distillation, is required for the recovery of the nicotine alkaloids. At these higher temperatures, more nicotine is thermally degraded as well as the generation of undesirable pyrolysis products from the tobacco material.[22]

CONFIDENTI

It was felt that for the nicotine recovery system to be operated economically, the method chosen should cause little or no injury to the tobacco material. This would allow the tobacco, after extraction, to be reused for blending into a low "tar", low nicotine blend.

Of the methods outlined, the two causing the least amount of damage to the tobacco are the water extraction technique and the organic solvent extraction technique.

Our preliminary investigations into the dry distillation of tobacco [23] and direct steam distillation of leaf material [24] were not encouraging. The nicotine recovery was very low and the processing resulted in partial or complete destruction of the leaf material. These procedures would not be applicable to the extraction of nicotine from reusable leaf material, however, they might find utility in the recovery of nicotine from stems, dusts, or sands.

Although there is an attractive patent making use of supercritical fluids [25] it was not possible to investigate the use of extraction techniques employing them due to the unavailability of the high pressure equipment need for a laboratory evaluation.

This report deals primarily with our investigations into the water extraction techniques and the extraction of nicotine from tobacco with organic solvents.

CONFIDENTIAL

Organic Solvent Extraction

The use of organic solvents to extract nicotine directly from tobacco has been well documented,[13] however, recently most of these solvents have been under investigation as to their adverse toxicological properties. If the tobacco is to be reused as a smoking material, the solvent residue levels remaining must be minimal and harmless.

Preliminary investigations into the choice of solvent included a isooctane/heptane system. The isooctane/heptane extraction system seemed to be only moderately efficient yielding only a 64% reduction in the leaf nicotine. The recovery of the nicotine from the solvent was excellent and produced an overall 63% recovery as the sulfate.[26]

The use of kerosene or gasoline would leave large hydrocarbon residues which would not only be highly flammable but might render the tobacco useless.

Based on a patented procedure[15] we investigated the methyl ethyl ketone - brine extraction system. A four-fold extraction of tobacco with methyl ethyl ketone extracted over 85% of the leaf nicotine. The methyl ethyl ketone was extracted with cold acidic brine. The brine extract was made alkaline with sodium hydroxide and warmed. This caused the nicotine to separate as a distinct upper phase which was separated. Upon analysis this phase was shown to be 20% nicotine giving a recovery of 82% from the leaf. In order to isolate the pure alkaloid a purification step would be required from this recovered concentrated nicotine upper phase.

The experimental details of this extraction and the isooctane-heptane extraction have been reported previously.[26] Methyl ethyl ketone, chloroform, methylene chloride, trichloroethane and dichloroethane have been shown to be, or are suspected of being, carcinogenic agents. Freon 11 offered a solution to this problem in spite of current environmental controversy. The low boiling point (24°C) would enable volatilization with a minimum of heat and leave a very minimal residue on the tobacco itself. Since we currently use freon 11 in our puffing process the technology for handling and recovering large volumes of this solvent from tobacco is readily available.

The following experiment, based upon a patented procedure,[14] was performed in order to determine the relative efficiency of nicotine extraction from leaf material by freon 11.

A 300g portion of Burley tobacco, Grade HH, was coarsely chopped and mixed with 60 ml of water. After standing for 30 minutes 1.75 ℓ of freon 11 was added. This suspension was allowed to stand for 30 minutes at 20°C then the tobacco was filtered through cheesecloth. After air drying in a hood for 24 hours the tobacco was then analyzed for nicotine content. The freon was extracted with two 25 ml portions of 30% aqueous citric acid solution and analyzed by capillary gas chromatography.[27]

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTIAL

The following table lists the results:

TABLE 1

Leaf Analysis of Freon Extracted Tobacco

Tobacco or Extract	% nicotine	% total nitrogen
Burley, Grade, HH	3.23	4.79
Grade HH, Extracted	3.30	4.67

The citric acid solution was found to contain 230 mg nicotine corresponding to ∿ 2% of the total leaf nicotine available. This correlates quite well with the amount of "free nicotine" found on burley tobaccos.[28]

One major deviation from the patented procedure was the use of 20°C at atmospheric pressure. The literature claims to have used 64°C at 40 psi.

This work indicated that freon 11 would not extract any appreciable amount of nicotine from the tobacco when used at room temperature and pressure. It was felt that the nicotine could be extracted if the tobacco were first treated with alkali strong enough to release "bound" nicotine. For this reason ammonia was chosen and the following series of experiments performed to roughly determine the relative amount needed for efficient extraction of the nicotine from the tobacco. For the ammonia study the solvent used was not freon but rather methylene chloride. Even though this solvent would not be used for our large scale extraction process the lower volatility and very similar extraction properties made it possible to rapidly analyze the extracts directly for nicotine without solvent volatilization errors or subsequent acid extraction error.

A 200g portion of coarsely chopped burley tobacco, was mixed with a solution of the desired amount of concentrated ammonium hydroxide (28.4% ammonia by weight, d = 0.90 g/ml) which had been diluted with water to 50.0 ml. After 30 minutes 500 ml of methylene chloride was added to the mixture. This suspension was allowed to stand for an additional 30 minutes in a covered beaker with no agitation. The solvent was filtered through cheesecloth and the tobacco pressed. The solvent was analyzed directly for nicotine.[27] The tobacco was air dried in a hood for 24 hours then submitted for leaf analysis.

The results of these series of experiments are listed in Tables 2 and 3.

The maximum extraction efficiency for this one extraction system, using a minimum of solvent, was reached when approximately 3.2g of free ammonia per 100g of tobacco was used at this 25% moisture level. This level corresponds to approxi-

CONFIDENTIAL

TABLE 2

Leaf Analysis of Tobacco after Sequential Increments of Ammonium Hydroxide

Tobacco	NH_4OH (ml)	NH_3 (mmol)	NH_3 (g)	% Nicotine
* 1. Burley Grade HH	-	-	-	3.25%
2. 200.0g	0	0	0	2.70%
3. 200.0g	10	150	2.55g	1.50%
4. 200.0g	18.8	280	4.76g	1.30%
5. 200.0g	25.0	375	6.37g	1.26%
6. 200.0g	31.6	475	8.08g	1.40%
7. 200.0g	40.0	600	10.20g	1.40%

* Starting Material - untreated

TABLE 3

Gas Chromatographic Analysis of Extracts

	NH_3 Added (mmol)	g nicotine/100g tobacco
1.	0	0.56
2.	150	1.61
3.	280	1.61
4.	375	1.91
5.	475	1.86
6.	600	1.71

CONFIDENTIAL

mately 18 fold molar excess based upon the relative amount of nicotine in the tobacco. Much of this ammonia is lost upon drying of the tobacco material since the total nitrogen increases by only 0.5% while the total volatile bases increases by about 0.3%.

These experiments have determined that the approximate amount of ammonia required to effectively alkalinize the tobacco for the maximum efficiency of extraction of the nicotine alkaloids is 2.8 - 3% of the tobacco weight as free ammonia at a 25% moisture level.

Before any large scale freon extraction was attempted more information was required to determine the optimum ratio of freon to tobacco in order to extract the most nicotine using the least quantity of freon.

In each experiment 100.0g of cut HL '75 Burley tobacco was mixed with a solution of 10 ml of concentrated ammonium hydroxide and 15 ml of distilled water. This mixture was allowed to stand in a covered beaker for 20 minutes then the desired amount of freon was added. The suspension was allowed to stand at room temperature (21°C) for 20 minutes then suction filtered. The tobacco was washed with an additional 100 ml of fresh freon and rapidly pressed as dry as possible. The tobacco was spread out in a hood and dried under an air stream for 24 hours before leaf analysis.

The following Table 4 shows the results of these experiments:

TABLE 4

Leaf Analysis and Recovery Volumes - Sequential Addition of Freon

liters FC-11 Added *	liters FC-11 Recovered *	Leaf Analysis	
		%nicotine recovery	%total nit.
@ -	-	3.39 @	4.21 @
1) 0.40	0.21 (53%)	1.18 (34%)	4.45
2) 0.60	0.39 (65%)	1.39 (41%)	4.40
3) 1.10	0.88 (80%)	1.05 (31%)	4.50
4) 1.60	1.36 (85%)	0.80 (24%)	4.27
5) 2.10	1.89 (90%)	0.85 (25%)	-

* Includes the 100 ml wash
@ Starting Tobacco analysis without ammonia treatment

As expected the freon recovery efficiency percentage increases with increasing amounts of added freon. In all cases ∿ 3 times the tobacco weight in freon remains absorbed on the leaf particles.

CONFIDENTIAL

Although this large amount of freon was absorbed it could be efficiently recovered by technology currently in use for our tobacco puffing process.

The minimum freon to tobacco ratio required for maximum extraction efficiency on one extraction is a 22.5 to 1 by weight or a 15 to 1 freon volume to tobacco weight.

The maximum leaf reduction we obtained on any freon-11/ammonia extraction system was 85%. These experiments were all performed on laboratory size equipment which might not accurately reflect either the total extraction and recovery efficiency or difficulties sometimes encountered upon increasing the size of the process.

A larger scale extraction was performed to determine "scale up" efficiency, to supply Ms. S. Ireland with approximately 1/2 lb. of nicotine extracted from our tobacco and to identify any associated problems.

A 25.5 lb. (11.58 kg) portion of cut burley tobacco, grade 7, was placed into a 30 gal. polyethylene settling tank which had the tap covered with wire screen. A mixture of 1 ℓ of concentrated ammonium hydroxide and 1.5 ℓ of distilled water was added. The tobacco was mixed with a large paddle until it appeared to be evenly moistened. The tank was covered and allowed to stand for 15 minutes. A 25 gal. (313 lbs.) portion of freon was added in 5 gal. lots and the tobacco-freon slurry was allowed to stand at ambient temperature (45°F, 7°C) for 2.5 hours without agitation. The freon was drained from the tank into another 30 gal. polyethylene settling tank and the tobacco washed with one 5 gal. portion of fresh freon. The freon extracts and wash were combined to yield a recovered 20 gal. (250 lbs.).

The tobacco was removed from the tank and a small representative portion was spread out and allowed to air dry in a hood for 24 hours. The tobacco was then sent for leaf analysis. The results of this analysis are listed in Table 5.

TABLE 5

Leaf Analysis of Tobacco from Large Scale Extraction I

Tobacco	% nicotine	% total nitrogen
Burley Grade 7	2.85	3.15
Burley 7 Extracted	1.58	3.59

This analysis indicates that only 45% of the nicotine present in the original tobacco was removed. A laboratory scale reaction with a freon/tobacco ratio of 12 to 1, as in the large scale extraction, effected a 68% reduction of the leaf nicotine.

CONFIDENTIAL

One major difference was in the amount of mixing. The smaller scale was easily stirred allowing a more uniform distribution of the ammonia solution. The temperature was also about 30°F (15°C) higher. This combination of higher temperature and more efficient mixing could allow better absorption of the ammonia by the tobacco and consequently better release of the nicotine.

Two separate isolation procedures were attempted to determine which would give the greatest recovery of the extracted nicotine alkaloids. The isolation procedures attempted were (1) direct distillation and (2) aqueous acid extraction.

(1) A 3 gal. portion of the freon extract was rotary evaporated to yield 65g of black semi-solid residue. This residue was vacuum distilled and 17.8g of pale yellow liquid was collected, b.p. = 110°-112°C/7 mm, leaving a 46.7g pot residue. The residue solidified upon cooling. Capillary GC analysis indicated the distillate was 94% pure nicotine.

(2) The remainder of the freon (17 gal.) was extracted portionwise using a total of 700 ml of 50% aqueous sulfuric acid. The nicotine sulfate solution was made strongly alkaline with technical sodium hydroxide and vacuum distilled. As shown in a later experiment the isolation of the pure alkaloid by this method was successful when applied to "Black Leaf 40", i.e. 40% nicotine sulfate solutions.

The distillate (104g) had a boiling range of 50°-70°C and was found to contain only 16% nicotine or 16.6g by capillary G.C. analysis.

The 104g of aqueous nicotine was fractionally vacuum distilled to afford 20.8g of pure alkaloids, b.p. = 117°-118°C/10 mm. The direct distillation technique gave by far a more efficient recovery of the nicotine alkaloids. The low efficiency of recovery in the second procedure could possibly be attributed to the concentration differences between Black Leaf 40, 40% nicotine sulfate, and our extracts, calculated to be approximately 16% nicotine sulfate with 200g of unreacted sulfuric acid. Upon treatment with sodium hydroxide the large amount of sodium sulfate which precipitated could prevent transfer of heat during the vacuum distillation or strongly occlude the nicotine.

In order to supply Ms. Ireland with 1/2 lb. of nicotine the extraction was repeated with certain modifications.

A mixture of 15.5 lbs. of cut Burley Grade 7, 3.5 lbs. of cut Burley Grade HL'75 and 8.5 lbs. of cut Burley Grade OH'73 was mixed portionwise with a solution of 1.3 ℓ concentrated ammonium hydroxide and 1.7 liters of water.

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTIAL

The ammoniated tobacco was allowed to stand at ambient temperature (0°C) for 24 hours. To this was added 27 gal. of FC-11 and the slurry was allowed to stand for 3 days.

The freon was drained from the tobacco and the tobacco washed with 5 gal. of fresh freon.

A small amount of the freon was spilled during the transfer from the extraction tank to the freon holding tank. The recovered extract and wash totaled 26 gallons. The entire extract was treated by the first procedure to more efficiently recover the nicotine alkaloids.

The 26 gallons were distilled from two 12 ℓ flasks portionwise until ∿ 3 liters remained in each flask. This was further concentrated in a 2 ℓ flask, by distillation, until 1.5 liter remained. The dark residue was vacuum distilled to afford two fractions, both containing substantial amounts of nicotine. The first fraction, b.p. = 111°-119°C/10 mm, amounted to 219.2g. This was given to S. Ireland for respraying onto tobacco along with the 20.8g from the previous extraction. The second fraction, b.p. = 120°-128°C/10 mm, amounted to 41.4g. Upon standing the first fraction became pale yellow whereas the second fraction turned light yellow/orange. Capillary G.C. analysis indicates the second fraction was contaminated with about 5% unknown volatiles.

A small representative sample of the tobacco was spread out and air dried in a hood overnight. The results of the leaf analysis are listed in Table 6.

TABLE 6

Leaf Analysis of Tobacco from Large Scale Extraction II

Tobacco	Weight (lbs.)	% nicotine		%total nitrogen	
Burley Grade 7	15.5	2.84	3.32% Ave. *	3.15	3.71% Ave. *
Burley Grade HL'75	3.5	3.39		4.21	
Burley Grade OH'73	8.5	4.17		4.54	
Mixed and Extracted	27.5	0.65		4.72	

* These average values are of the entire mixed sample based upon the relative amounts of each tobacco in the mixture.

The leaf analysis indicated that 80% of the contained nicotine was removed. The total nicotine recovered amounts to 258.5g nicotine or 62% of the total leaf nicotine available before extraction. This gives a recovery efficiency of 78% from the freon.

CONFIDENTIAL

The freon 11 ammonia extraction technique appears to be generally applicable to a large scale process. The long reaction time required for the 80% extraction observed here could possibly be shortened by agitation and somewhat higher temperatures. The extreme volatility of the freon made it undesirable to operate at higher temperatures using the present equipment.

The aqueous acid workup would still seem like a viable concentration route. Possibly a series of scrubbers could be used to bring the nicotine sulfate concentration to 40% before the scrubbing efficiency dropped below acceptable limits.

One problem encountered in the large scale freon extraction of tobacco was the large amounts of non-alkaloid freon solubles. From the 27.5 lbs. of tobacco processed the residue weighed slightly over 850g (7% by weight). Upon workup only 29% of this material was found to be nicotine. This means that 5% of the tobacco material by weight which is not nicotine is soluble in the freon.

It might be desirable to readd this 5% by weight of non-alkaloid freon solubles since they might contribute a number of valuable natural flavoring materials.

A possible solution to this residue problem would be a pre-extraction of non-alkalinized tobacco to remove most of the freon solubles, then ammonia treatment and re-extraction to remove the released nicotine.

It was shown previously that freon 11 extraction of tobacco would not remove any substantial amount of the entrained nicotine. The following experiment was performed in order to determine the relative amounts of non-alkaloid materials which could be extracted with freon 11. By pre-treating the tobacco with freon the tobacco should remain saturated and allow use of a smaller volume of freon for nicotine extraction.

A 100.0g portion of cut Burley, Grade 7, was mixed with 1 ℓ of freon 11 and allowed to stand for 30 minutes. The freon was suction filtered off the tobacco. The 800 ml of recovered freon (80%) was rotary evaporated to yield 3.3g of viscous semi-solid residue.

The tobacco was then treated with a mixture of 10 ml of concentrated ammonium hydroxide and 15 ml of water and allowed to stand for 20 minutes. To this mixture was added 1 ℓ of fresh freon 11 and the slurry was allowed to stand for an additional 20 minutes. The freon was suction filtered off the tobacco. The tobacco was pressed dry and washed with 100 ml of freon. The 900 ml of recovered freon (82%) was rotary evaporated to yield 3.60g of dark viscous oil.

CONFIDENTIAL

The tobacco was air dried in a hood for 24 hours then sent for leaf analysis.

The following Table 7 summarizes the results found in this experiment:

TABLE 7

Leaf Analysis of Tobacco from Two-Stage Extraction

Tobacco	% nicotine	% nitrogen
Burley Grade 7	2.85	3.15
Grade 7 Extracted	0.45	4.44

The leaf analysis results show that 84% of the nicotine was extracted from the tobacco. The capillary gas chromatographic analyses of the two extracts agreed with the previous freon extraction experiments and indicated that the majority of the nicotine (>95% of the total extracted) was extracted only after treatment with ammonia.

The pre-extraction technique can be used successfully to lessen the amount of non-nicotine extractables in the final nicotine recovery process. A large scale technique could involve two distillation steps, requiring additional heating and cooling costs. The advantage would be in the purer fraction of nicotine, possibly not requiring a final distillation to be suitable for augmenting low tar low nicotine tobacco. The procedure may more readily allow for the isolation of valuable natural flavorants from waste or scrap tobacco as well as from reusable smoking tobacco.

Waste stems that are not used in the reconstituted leaf process, are a large source of waste tobacco material for use as a nicotine source. The following experiment was performed in order to roughly determine the applicability of the freon 11-ammonia extraction procedure to the recovery of nicotine from these stems. The dry stems were received from the Louisville stemming operation.

A 1000g portion of coarsely chopped stems was treated with a solution of 150 ml of water and 100 ml of concentrated ammonium hydroxide and stirred until the mixture appeared evenly moistened. The mixture was covered and allowed to stand at room temperature for 30 minutes. A 5.5 ℓ portion of freon 11 was added and the suspension was allowed to stand without agitation at 21°C for 1 hour covered with a glass plate.

The freon was drained off through a wire screen and upon evaporation afforded 15.8g of residue. (4.9 liters recovered)

The stems were spread out and air dried in a hood for 24 hours.

TABLE 8

Leaf Analysis of Stems from Freon Extraction

Tobacco	% nicotine	% nitrogen	TVB
Waste Stems	1.05	2.94	0.76
Stems - Extracted	0.55	2.90	0.91

It can be seen that there was a 48% reduction in nicotine in the stems using the freon extraction technique. The stems were very dry and very compact. The 5.5 ℓ of freon 11 used covered the stems, although, they had a tendency to float and the top portion was not under the freon surface.

The large fraction of the freon recovered (89%) suggests that the compactness of the stems prevented good absorption and therefore prevented good dissolution of the entrained nicotine.

With the use of stems it can be seen that most of the 2.6% added ammonia was not retained by the tobacco material. Only about 0.15% by weight was absorbed compared to ∿ 0.7% by weight retained on whole or cut burley leaf.

The fact that there was no apparent change in total nitrogen can be explained. The 0.50% of nicotine extracted accounts for a decrease in total N by 0.09%. If the 0.15% TVB increase were all added ammonia, the total N increase would be 0.12%. The overall change in total N would therefore be 0.03%. This is within the experimental error of the determination.

Relative to the 80% reduction of total nicotine in leaf or cut tobacco the stem extraction is less efficient (48%). The parameters of this FC-11-ammonia technique could be changed to determine if a higher efficiency can be obtained. Possibly a higher moisture would allow better transfer of the nicotine. More agitation, high temperature and pressure for better solvent penetration or a finer cut stem material might also effect a more efficient extraction of the nicotine from stems.

CONFIDENTI

In order for the freon/ammonia extraction technique to be economically feasible for the isolation of nicotine, from leaf material purchased specifically as a nicotine source, the tobacco should remain a usable smoking material.

Expert evaluation of tobacco from which 85% of the nicotine had been removed was not encouraging. The following Table 9 lists the taste profile for tobacco which had been extracted with freon. The nicotine was extracted from the freon by washing with two 50 ml portions of 10% sulfuric acid solution and the non-alkaloid freon solubles were diluted in ethanol. Half of this solution was replaced on half of the extracted tobacco.

TABLE 9

Taste Profile of Freon-Ammonia Extracted Tobacco

Tobacco	Nicotine (%)	Taste Evaluation[29]
(a) Burley OH'73	3.95	Good character, strength and body
(b) Burley Extracted	0.47	No character, no strength no body, burnt, smoky bitter off-taste
(c) Burley Extracted and Resprayed with "Flavor Fraction"	0.57	No character, no body, slightly more strength same off-taste as (b) but less intense

Without further processing the tobacco is not suitable as a smoking material. It was theorized that an alternate nicotine releasing agent might impart a suitable flavor and/or allow easier removal of the alkalinizing reagent.

This experiment was performed using both a minimal amount of freon for partial nicotine extraction and an equal weight percentage of amine to nicotine to lessen the off'taste.

A 100.0g portion of cut Burley, Grade 7, was mixed with 5 ml of 40% aqueous methylamine and 20 ml of water. This was covered and allowed to stand for 20 minutes. A 300 ml portion of freon was added and the slurry allowed to stand for an additional 20 minutes.

The freon was suction filtered from the tobacco. The 90 ml of recovered freon (30%) was rotary evaporated to yield 2.80g of viscous residue. The residue was taken up in 100 ml of 95% ethanol and analyzed by capillary G.C. to indicate 1.34g (47%) of nicotine had been extracted.

CONFIDENTIA

The tobacco was air dried overnight in a hood and sent for leaf analysis. Table 10 lists the results of the leaf analysis.

TABLE 10

Leaf Analysis of Methylamine - Freon Extracted Tobacco

Tobacco	% nicotine	% nitrogen
Burley Grade 7	2.85	3.15
Grade 7 Extracted	1.50	4.61

No formal evaluation of this tobacco has been completed. Preliminary smoking results indicated the tobacco still retained the burnt, bitter off-taste however was less objectionable. The methylamine seemed to impart a cigar/pipe taste to the tobacco. Since less methylamine was used than ammonia only 47% of the nicotine was extracted. It is not known whether the altered taste was due to less amine added and less nicotine removed or rather to the alternate amine added for alkalinization.

The methylamine seems to bind somewhat more to the tobacco than does ammonia since the total nitrogen on analysis was over 0.5% larger than when ammonia is used.

Conclusions to Freon Work

1. The freon 11-ammonia extraction technique is a viable method for the efficient (80-85%) removal and recovery of nicotine from tobacco materials. Maximum extraction efficiency can be obtained by using 2.8-3% by weight of free ammonia and a 15 to 1 ratio of freon to tobacco.

2. The use of a sequential or "two-fold" extraction technique is desirable, in which the first extraction removes the "Flavor fraction" and the second extraction, after ammonia treatment, removes the nicotine. This "flavor fraction", as well as the nicotine to be used for augmentation, could be recovered from currently discarded tobacco waste affording potential natural flavor additives as byproducts.

3. The direct distillation of the freon extracts, either from the one extraction technique or from the sequential extraction process, affords the most efficient recovery of the pure nicotine alkaloids.

4. The dramatic change in the flavor characteristics of the tobacco when methylamine was used as the alkalinizing agent suggests that R & D operations might solve the off-taste problem associated with the ammonia treatment by the selection of an alternate reagent or additional processing of the ammonia treated tobacco.

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTI

Recommendations for Freon Extraction

1. It is recommended that flavor R & D work with the ammonia treated tobacco be performed to determine if it is possible to obtain a suitable smoking product.

2. Pressure extraction studies to determine if 20-40 psi and better agitation would significantly improve the 80-85% extraction efficiency and decrease the time required for each extraction in this batchwise process.

3. Adaptation of a continuous process freon-ammonia extraction technique to minimize time required for the total amount of tobacco extracted.

4. Sequential sulfuric acid scrubbing towers, or an alternate aqueous acid concentration step, to form the high concentration of nicotine salt solution to be used for alkaloid recovery, or for direct augmentation of low nicotine, low "tar" tobaccos. The nicotine salt solutions would slightly decrease the hazards associated with transportation and application of the pure alkaloid.

5. Contact corporations associated with liquid-solid extraction techniques and determine the availability of technical consultation in the extraction of nicotine from tobacco for our use, i.e. French Oil Mill Machinery Company.

6. Investigation into the utilization of any isolated "flavor fraction" from the two stage extraction process.

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTIAL

Water Extraction

Waste tobacco has been used as a commercial starting material in the manufacture of "Black Leaf 40" insecticide by successive extraction of the nicotine from the tobacco with water. The dilute aqueous nicotine solutions are then concentrated by high pressure steam distillation into aqueous sulfuric acid.[11] Unlike the organic solvent extraction procedures, the only residue left on the tobacco was water which did not require recovery for an economical process.

It was felt that we could use this technique to extract tobacco wastes and recover the nicotine for use in augmentation. Additionally, a high nicotine tobacco could be purchased and processed in a similar manner without excessive injury to the tobacco. The tobacco could be reused in a low "tar", low nicotine blend of tobaccos after drying.

Preliminary experiments were performed using cut Burley and cut Flue-cured tobaccos in the sequential extraction technique. These experiments were designed to determine the overall extraction efficiency as well as to give a rough indication of the amount of damage to the tobacco.

I. Burley Extraction

A total of 500.0g of HL '75 Grade cut Burley was extracted in five 100.0g portions. Each 100.0g portion of tobacco was extracted five times with 500.0 ml of water each time in a successive extraction scheme. The following Table 11 represents the extraction pattern and the recovery volumes. The water was separated from the tobacco by draining through a wire screen.

TABLE 11

Sequential Extraction Scheme for Small Scale Burley Tobacco

TOBACCO ADDED	WATER AND FRACTION ADDED	WATER RECOVERED	FRACTION NUMBER
1. 100.0g	500 ml	180 ml	1A
	500 ml	440	1B
	500 ml	490	1C
	500 ml	475	1D
	500 ml	620	1E
2. 100.0g	1B + 60 ml	200 ml	2A
	1C + 10 ml	440	2B
	1D + 25 ml	500	2C
	1E	530	2D
	500 ml	500	2E
3. 100.0g	2B + 50 ml	240 ml	3A
	2C	490	3B
	2D	500	3C
	2E	600	3D
	500 ml	600	3E

CONFIDENTIAL

TABLE 11 (continued)

TOBACCO ADDED	WATER AND FRACTION ADDED	WATER RECOVERED	FRACTION NUMBER
4. 100.0g	3B + 10 ml	280 ml	4A
	3C	440	4B
	3D	500	4C
	3E	500	4D
	500 ml	540	4E
5. 100.0g	4B + 60 ml	240 ml	5A
	4C	450	5B
	4D	500	5C
	4E	500	5D
	500 ml	620	5E

The fractions, 1A, 2A, 3A, 4A, 5A, B, C, D and E were combined to yield 3210 ml of a dark solution. To this was added 200 ml of 50% sodium hydroxide solution and this mixture was distilled as rapidly as possible to yield 3250 ml of a clear yellow solution. Analysis by capillary GLC indicated 11.3g (78%) of nicotine was recovered.

The distillate was brought to pH ~4 with concentrated sulfuric acid and evaporated on a hot plate to 25 ml. Upon cooling the black solution partially crystallized. Addition of 10 ml of distilled water brought the solids back into solution.

The tobacco was air dried for 4 days in a hood then at 40°C for 24 hours in a constant temperature drying room (Pilot Plant). This tobacco was slightly broken up but upon cursory examination seemed to be a smokable product.

II. Flue-Cured Extraction

A 500.0g portion of cut VLO'73 Flue-cured tobacco was successively extracted using an identical sequence. The water and extracts were brought to 60°C ± 5°C, added to the tobacco and the temperature maintained for 20 minutes. The liquid was drained off the tobacco using a wire screen. The extracts contained 5.0g (88%) of nicotine by capillary GC analysis. These extracts were not worked up.

In these extraction experiments the extracts must be processed as soon as possible. Bacterial degradation of the nicotine begins almost immediately as evidenced by mold formation and noticeable frothing within 24 hours. This degradation was more pronounced in the flue cured extracts, possibly due to sugar fermentation.

CONFIDENTIA

The Table 12 shows the analytical results obtained by comparing the burley and flue-cured tobaccos before and after sequential water extraction.

TABLE 12

Leaf Analysis of Sequentially Extracted Burley and Flue Cured Tobacco

Tobacco	% Nicotine	% Total Nitrogen	Sugars
HL '75 Burley	3.39	4.21	0
HL '75 Burley Extracted	0.55	2.87	0
VLO'73	1.38	1.95	11.50
VLO'73 Extracted	0.24	2.09	0.90

There was a nicotine extraction efficiency of 84% from the cut burley tobacco and 83% from the cut flue cured. In the flue cured extraction, however, over 92% of the total reducing sugars were also extracted. In the burley tobacco, which did not have this problem initially having little or no reducing sugars, the total nitrogen loss in the burley tobacco was 32% of which only 11% was attributable to the loss in nicotine nitrogen. This means that the remaining 21% of the nitrogeneous materials were water extractable. The loss of these additional non-alkaloid compounds from both types of tobacco might present either problems in the recovery of the nicotine or organoleptic problems with the tobacco.

Another potential problem is the fact that, the tobacco rapidly "soured" when air dried. Any large scale operation should include a method for rapid drying. The cut tobacco drier in the pilot plant dried the tobacco but required 4 passes and broke the fibers.

This extraction method was highly efficient for extracting nicotine in these small scale determinations. In order to determine any problems which might be encountered upon increasing the scale this extraction scheme was repeated with a larger quantity of cut burley tobacco.

In this experiment 10 lbs. of OH-73 cut Burley (4.17% nicotine, 4.54% total nitrogen) was divided into 2 lb. lots. The first 2 lbs. was extracted at room temperature with 5 one gallon portions of water. The extraction vessel was a 6 gal. polyethylene tub equipped with a drainage tap and a wire mesh on the bottom. The mesh served to strain the water from the tobacco and prevent clogging of the tap. In each extraction the tobacco was soaked for 30 min. with

CONFIDENTIAL

occasional stirring. The first extract was set aside and the other 4 reused as extracts for the next 2 lbs. of tobacco with the addition of a fresh gallon of water in the fifth extraction. This type of sequencing was repeated with subsequent lots of tobacco, each time setting the first extract aside. Table 13 gives the order of this sequencing with initial and drainage volumes of each extract. When a drainage volume was less than 1 gal. the extract was topped off to 1 gal. before reuse. Additionally, 1.25 gal. were used in all first extracts to compensate for water loss through absorption by the tobacco. Extracts A-1 through A-5 were combined to give 2 gal. of "primary extracts" and the rest combined to give 4 gal. of "secondary extracts".

After extraction the tobacco was dried for 18 hours at 45°C and 4 hours at 110°C. Leaf lab analysis showed the nicotine content had been reduced to 0.66% (an 84% reduction). The concentrations of the first five extracts of this sequence were roughly determined, by capillary vpc analysis, to find the relative efficiency for each extraction. Table 14 shows that the extraction efficiency is over 49% after the second extraction. It was theorized that a large quantity of the nicotine was extracted on the first extraction and the other four extractions partially act to wash the nicotine from the water absorbed onto the tobacco.

An experiment was performed in which only one extraction was used but the initial water volume to tobacco ratio was greater. This large volume of water would allow better washing of the nicotine from the large amount of water absorbed by the tobacco but yield a more dilute solution of nicotine.

Since the extraction was performed only once there was less manipulation of the cut leaf particles and less chance that this material would be excessively broken up.

A high nicotine tobacco such as HH or OH Burley could have the nicotine partially extracted and still be suitable for blending. The extracted nicotine could then be isolated and added to another blend to augment a high nicotine brand.

A 5 1/2 lb. portion of cut OH '73 Burley tobacco was mixed with 4 gallons of water. The suspension was allowed to stand at room temperature (22°C) for 1 hour then the tobacco was drained, using a wire screen, to yield 3 gallons of liquid.

CONFIDENTIAL

TABLE 13

Sequential Extraction Scheme for Large Scale Burley Tobacco

2 lb. lot	Extract	Initial Vol.[a]	Drainage Vol.[b]	Nicotine Conc.[c]
1	A-1	1.25	0.25	4.56
	A-2	1.0	1.0	3.72
	A-3	1.0	1.0	2.18
	A-4	1.0	0.9	0.54
	A-5	1.0	1.0	0.14
2	A-2	1.25	0.3	
	A-3	1.0	1.0	
	A-4	1.0	1.0	
	A-5	1.0	0.9	
	B-1[d]	1.0	1.0	
3	A-3	1.25	0.4	
	A-4	1.0	1.0	
	A-5	1.0	0.9	
	B-1	1.0	0.9	
	C-2[d]	1.0	1.0	
4	A-4	1.25	0.5	
	A-5	1.0	1.0	
	B-1	1.0	1.0	
	C-2	1.0	1.0	
	D-3[d]	1.0	1.0	
5	A-5	1.25	0.5	
	B-1	1.0	0.9	
	C-2	1.0	1.0	
	D-3	1.0	0.9	
	E-4[d]	1.0	1.0	

a) gallons
b) gallons
c) g/ℓ determined by capillary gas chromatography
d) fresh water

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTIAL

TABLE 14

Recovery of Nicotine from Sequential Extraction

Tobacco	Recovered Water	Concentration of Nicotine	total H_2O Nicotine	Extraction Efficiency
907.18g	0.95 ℓ	4.56 g/ℓ	4.3 g	11%
	3.79 ℓ	3.72 g/ℓ	14.1 g	49%
	3.79 ℓ	2.18 g/ℓ	8.3 g	71%
	3.41 ℓ	0.54 g/ℓ	1.8 g	75%
	3.79 ℓ	0.14 g/ℓ	0.5 g	78%

The water was analyzed by capillary g.c. and found to have a concentration of 4.5 g/ℓ. This amounts to 52.2g of nicotine recovered.

The tobacco was dried for 4 days at 40°C then 18 hours at 100°C. The dry Tobacco had the following analysis:

TABLE 15

Leaf Analysis of Tobacco from Partial Extraction

Tobacco	% Nicotine	% Total nitrogen
OH '73	4.17	4.54
OH '73 extracted	2.07	3.56

The extracted tobacco contained 50% of the original amount of leaf nicotine with 52.4g total being lost.

The tobacco fibers are not broken up; however, the large amount of water promotes fermentation and the material rapidly "sours".

It was not known whether the degradation of the tobacco was caused by the extraction of some fermentation inhibitor by the water, the release of fermentation promoting enzymes by the cutting process or a large increase in the natural fermentation rate of tobacco due to the large volume of water remaining on the tobacco during the slow drying process used here.

A rapid drying apparatus which might be applicable to this problem is the whole leaf drier. Currently the whole leaf burley tobacco is channeled through a "burley dip" tank and the very wet cased tobacco is efficiently dried without damage. This apparatus could be used immediately after the extraction of whole leaf material, with either the sequential process or the one extraction partial-nicotine reduction process. In this case the water would remain in contact with the tobacco

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTIAL

only during the extraction and would not remain to promote the fermentation processes. Additionally, the tobacco would not require a pre-cutting step and might minimize the particle breakage during extraction.

An extraction experiment was performed using whole leaf burley tobacco to determine the extent of the damage to the tobacco. The one extraction-partial nicotine reduction procedure was used in order to minimize manipulation of the tobacco and still allow the tobacco to be cut after drying.

A 5 lb. portion of the blend of burley tobaccos known as Kent Burley was placed into a 30 gal. polyethylene tank equipped with a drainage tap covered with a wire screen. Five gal. of water (25°C) was added and the slurry was agitated by stirring carefully for 20 minutes. The water was drained off through the tap and the leaf material squeezed gently to remove most of the absorbed water. Approximately 4 gal. of water (80%) was recovered. The tobacco was removed from the tank and dried by two methods: (a) air drying in a hood and (b) a Burley drying oven. A one lb. lot was spread out on a tray in a hood and air dried for 3 days. Surprisingly, no outward signs of decay were noticed during this time unlike the use of cut tobacco. The remaining four lb. sample was passed through a small whole leaf burley drier four times until the tobacco was as dry as possible. The following Table 16 indicates the results obtained upon leaf analysis of the tobacco.

TABLE 16

Leaf Analysis of Tobacco from Whole Leaf Partial Extraction

Tobacco	% nicotine	% total nitrogen
Kent Burley	2.95	3.95
Kent Burley Extracted	1.61	3.58

This analysis shows that 44% of the nicotine originally present in the leaf was extracted in this experiment.

Based upon this analysis the aqueous extracts should have a concentration of 0.20%. In order to avoid fermentation problems a 100 ml portion of chloroform was added and the solution was analyzed after standing for 8 days at room temperature. The concentration was found to be only 0.02% in nicotine by capillary vpc. The appearance of molds at the surface of the solution, and the low concentration of nicotine found upon analysis suggests that the added chloroform did not effectively inhibit bacteriological degradation processes in the extracts.

CONFIDENTIAL

The heater dried tobacco and air dried tobacco, as well as a sample of unextracted tobacco, were cut and sent for expert panel taste evaluation.[31] The results are listed in Table 17. The extracted tobacco was found to be superior to the original material. Even though no observable damage was seen, the air-dried material was less desirable than the heater-dried sample.

TABLE 17 [31]

Organoleptic Evaluation of Partially Extracted Kent Burley

	Tobacco	Taste Profile
A)	Kent Burley	Medium strength and character, burnt smoky off-taste
B)	Kent Burley Extracted (Burley Drier)	Slightly milder than A with medium character and slight burnt taste
C)	Kent Burley Extracted (Air Dried)	Medium strength and character with slight burnt taste

Order of Preference B > C > A

One of our largest quantity of tobacco wastes is the stems unfit for the manufacture of reconstituted leaf (RL).

It was necessary to ascertain the viability of the water extraction technique as a source of nicotine from waste stems. A sample of such stems (1.07% nicotine) was obtained from the Louisville plant and processed.

The manner in which this extraction was carried out was similar to that outlined previously on extraction of nicotine from burley tobacco. Due to the greater density of stems it was anticipated that their extraction would prove more difficult. Therefore, the following changes in the procedure were made:

1) The extraction was carried out at 75°-80°C instead of at room temperature. This was accomplished by passing steam through a copper coil inserted into the extraction mixture.

2) The extraction time was extended from 30 min. to 1 hour.

3) A slightly larger volume of water was used in the initial extractions.

CONFIDENTIAL

Ten lbs. of dry stems were extracted in separate 2 lb. lots. The aqueous extracts were sequenced through the individual lots as shown in Table 18.

Extracts A-1 through A-5 were combined as the primary extracts and the remainder as the secondary extracts. Leaf Lab analysis of the extracted stems showed a nicotine content of 0.15% indicating that 86% of the nicotine had been removed.

This experiment has shown that extraction of stems can be considered a viable potential source of nicotine. The disadvantages of stems vs. tobacco are three-fold: longer extraction times, higher temperatures, and more dilute extraction solutions. This is due to the highly compacted nature of the stems which makes it difficult for the solvent to reach the inner portion of the dry material.

The aqueous nicotine solutions generated by the water extraction technique have been worked up by high pressure steam distillation into sulfuric acid.[11] One reported method[32] of recovery, the nicotine as the pure alkaloid, has been the neutrallization of the nicotine sulfate solution with lye followed by a fractional vacuum distillation.

Before attempting any workup of the large amounts of dilute aqueous nicotine solution obtained in our water extraction methods it was necessary to determine the feasibility of recoverying the alkaloids from the nicotine sulfate solution.

A 60.0g portion of commercial Black Leaf 40 was cautiously treated with 25 g of powdered sodium hydroxide. This semi-solid was vacuum distilled through a 15 cm vigreaux column for 6 hours until all water had ceased distilling (pot temperature 125°C, unwrapped column). The column was removed and the nicotine vacuum distilled as a clear colorless liquid, b.p. = 110°-117°C/12 mm. The 21g (88%) of product was >99% pure by G.C. and turned pale yellow within 3 days at room temperature. No appreciable amount of nicotine was found in the water which distilled first.

The reported use of superheated steam to distill over the nicotine adhering to the sodium sulfate and condenser could bring the recovery much higher.

It was interesting to note that when the lye and the dark nicotine sulfate solution was mixed the color was black. Upon distillation the clear nicotine distilled and the sodium sulfate residue was left as white crystals. This suggests that it is not possible to determine the purity of these nicotine sulfate solutions based entirely upon the color of the mixture.

CONFIDENTIAL

TABLE 18

Sequential Extraction Scheme in Stem Extraction

2 lb. lot	Extract	Initial Vol. (gal)	Drainage Vol. (gal)
1	A-1	1.5	1.0
	A-2	1.0	0.9
	A-3	1.0	0.9
	A-4	1.0	0.9
	A-5	1.0	0.9
2	A-2	1.25	0.8
	A-3	1.0	0.9
	A-4	1.0	0.9
	A-5	1.0	0.8
	B-1	1.0	0.8
3	A-3	1.1	0.75
	A-4	1.0	0.8
	A-5	1.0	0.6
	B-1	1.0	0.6
	C-2	1.0	0.6
4	A-4	1.25	0.6
	A-5	1.0	0.8
	B-1	1.0	0.8
	C-2	1.0	0.9
	D-3	1.0	0.9
5	A-5	1.25	0.7
	B-1	1.0	0.9
	C-2	1.0	0.9
	D-3	1.0	0.9
	E-4	1.0	0.9

CONFIDENTIA

An alternate method was the extraction of the nicotine alkaloid with an organic solvent from the neutralized 40% nicotine sulfate solutions. A 20g portion of a 40% nicotine sulfate solution was treated with 10g of powdered sodium hydroxide and cooled in ice. The semi-solid was extracted 4 times with 50 ml portions of ether. The separation was difficult due to emulsion formation. The extracts were combined and rotary evaporated to yield 1.40g alkaloid (97% pure by G.C.). This amounted to a recovery of only 28%.

Of the two methods, it was apparent that the direct fractional vacuum distillation technique yielded a far better recovery, 88% compared to 28% efficiency, with a product of slightly higher purity.

With these results in mind the water extracts were processed to recover the nicotine.

Capillary vpc analysis of primary and secondary extractions, recovered from the sequential extraction of 10 lbs. of cut burley tobacco, indicated nicotine concentrations of 8.56 and 3.06 g/ℓ.

The initial step in the workup of the aqueous extracts was steam distillation of the nicotine into sulfuric acid traps. The distillation was carried from a 12 ℓ 3 neck round-bottom flask equipped with a steam inlet (sparging tube), thermometer and outlet. In hopes of facilitating the distillation the steam was passed over a heated nichrome wire coil within an insulated Vycor tube prior to introduction into the distillation pot. This arrangement served to heat the steam to approximately 150°C. The outlet passed into two traps, each containing 500 ml of 50% H_2SO_4. The distillation vessel was warmed via heating mantle to the degree necessary to maintain constant volume. (See Diagram 1)

The efficiency of this atmospheric steam distillation in terms of time, energy and overall nicotine removal was not acceptable. In distilling the primary extracts only 75% of the nicotine was removed in 12.5 hrs. This efficiency can be markedly increased by the use of steam at high pressure.

In order to compare the efficiency of atmospheric and pressurized steam distillations the flow rate of the atmospheric system used in these laboratories was calibrated. On a kg (of steam)/ℓ (of extract)/hr basis a reported[11] pressurized distillation was conducted at a rate 5.6 times faster than our atmospheric distillation. The parameters of the distillations are listed in Table 19.

CONFIDENTIAL

TABLE 19

Parameters of Steam Distillations

	Pressurized(1.7 atm)[11]	Atmospheric
Initial Nicotine conc. (g/ℓ)	8.18	8.71
Time(hr)/75% Completion	1.25	12.5
Steam flow (kg/hr)	60	1 @
Volume (ℓ) of extracts	81.8	7.5
Adjusted flow (kg/ℓ/hr)	0.73	0.13
Relative flow	5.6	1

@ Measured as condensed water

The major differences between the two methods are the relative flows and time necessary to reach 75% completion. The pressurized distillation was 10 times as fast at 5.6 times the flow rate. Thus, a 1.8 fold increase in efficiency can be achieved by raising the pressure 0.7 atm. It would seem likely that any industrial process would be carried out at even higher pressures to reduce the time required for an efficient distillation.

The nicotine sulfate produced from our steam distillation was made alkaline with technical sodium hydroxide. The sodium sulfate was filtered off and the aqueous solution distilled under aspirator vacuum (11-15 mm). Vpc analysis of the distillate indicated that 4g (2% overall yield) of nicotine was received.

The aqueous extraction of nicotine from tobacco has been shown here to be an efficient process. Major problems have been encountered, however, in the workup of the resultant solutions. The atmospheric pressure steam distillation used in this experiment is not a viable method for producing large amounts of nicotine sulfate. With the equipment on hand it would be impossible to conduct an adequate test of the high pressure steam distillation.

The neutralization of the nicotine sulfate and subsequent distillation resulted in a very low recovery of nicotine. Although analysis of the steam distillation pot residues indicated that a minimum of 58g of nicotine had been distilled, only 4g was recovered from the workup.

CONFIDENTIAL

Steam Distillation Concentration Apparatus

00778314

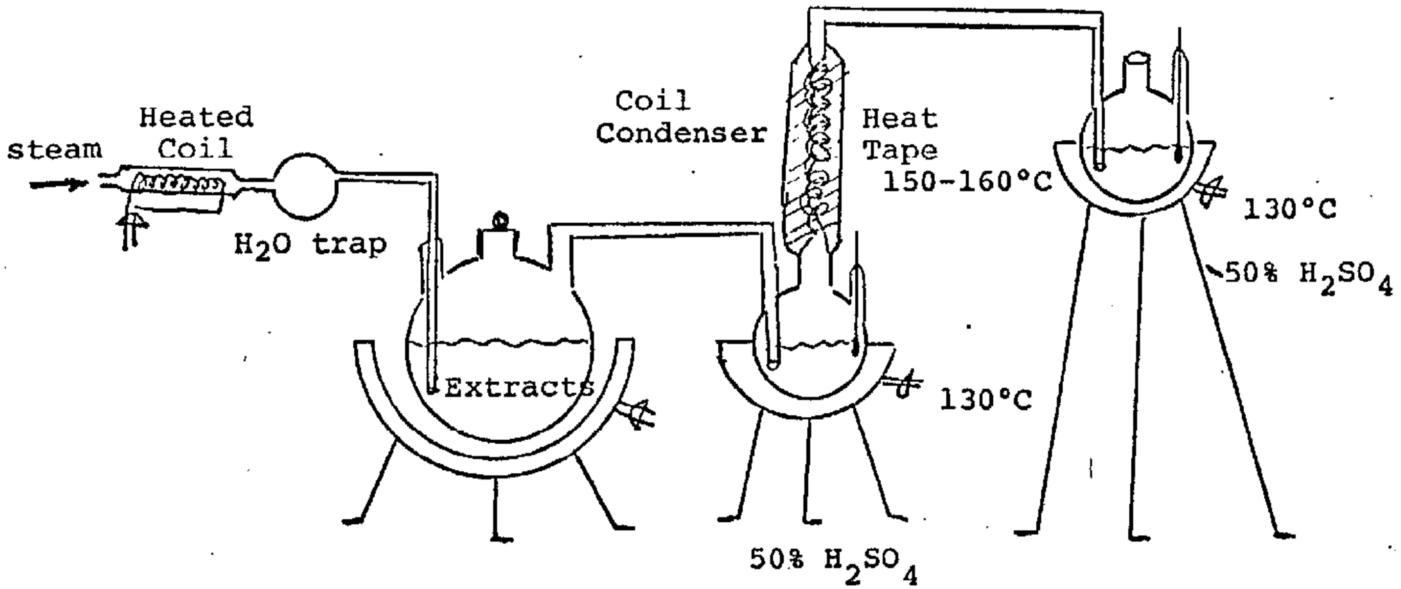


DIAGRAM 1

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

The reason for the extremely low recovery may be related to the much greater amount of sodium sulfate formed in these solutions. The nicotine sulfate concentration was around 5-8%, the remainder being sulfuric acid, ammonium sulfate, and water. When neutrlized with sodium hydroxide the nicotine to sodium sulfate ratio was much smaller than when 40% nicotine sulfate was used. The nicotine could have adhered to the sodium sulfate and been discarded upon filtration or there could have been difficulty in heat transference through so large a quantity of solids.

Two alternate methods of processing the dilute aqueous nicotine solutions are currently under investigation. These methods are (1) organic solvent extraction and (2) direct fractional vacuum distillation.

(1) The organic solvent extraction technique has previously been shown to be extremely efficient when dichloroethane is used.[33] The process involves the use of a continuous extraction tower filled with solvent through which the aqueous extracts are passed. The nicotine is concentrated in a continuous distillation stage of the organic solvent. (See Diagram #2)

It was felt that since the nicotine would be reapplied onto a smoking product to augment a low "tar" brand there must not be any appreciable amount of residue left in the nicotine. For this reason the organic solvent currently being investigated is Freon-11. The freon could be recycled and the nicotine concentrated to the desired level in the distilled.

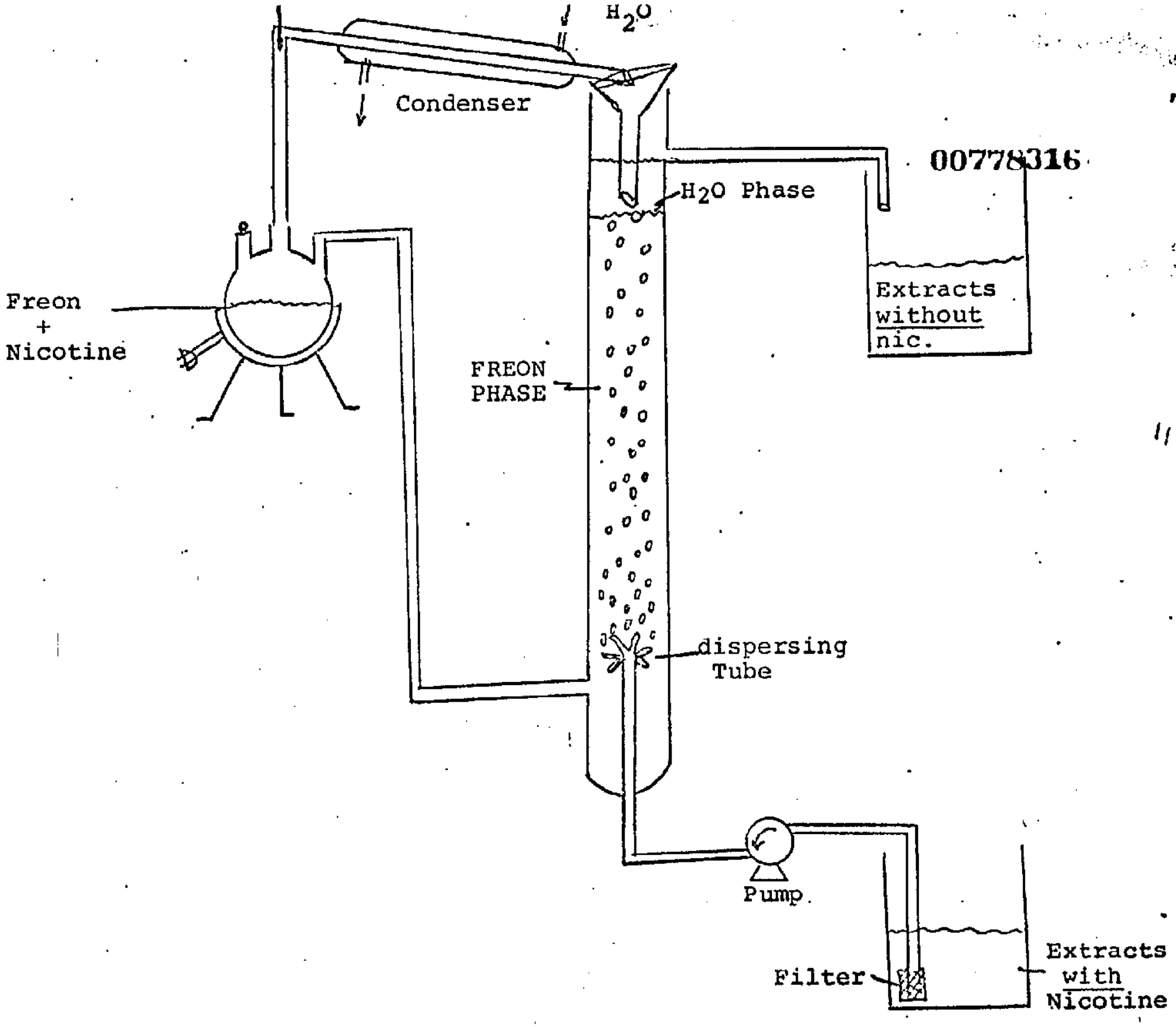
(2) The direct fractional vacuum distillation method could be used to concentrate the dilute solutions to an acceptable level, i.e. 50-80%, which could either be processed for the pure alkaloids by continued distillation, or used directly for augmentation.

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTIAL

DIAGRAM #2

Continuous Nicotine Extraction Equipment



CONFIDENTIAL

Conclusions to Water Extraction

1. The water extraction technique is an efficient method for the extraction of 80-85% of the nicotine from waste leaf, stems or high nicotine burley. This technique can be successfully applied to either partially or almost totally reduce the nicotine content of the tobacco without subsequent injury to the leaf material.

2. The use of whole leaf burley tobacco and the burley drying ovens affords a feasible method for the recovery of the tobacco as a usable smoking material of comparable quality to unextracted leaf. The advantages of whole leaf over cut tobacco include less tobacco souring, less breakage of the leaf and more rapid drying.

Recommendations to Water Extraction

1. The use of high pressure distillation equipment should be investigated. The high pressure distillation technique could possibly be used to concentrate the nicotine either as the sulfate salt or as a pre-concentration step for solvent extraction, to eliminate problems caused by many of the dissolved impurities in the original aqueous extracts.

2. The majority of the nicotine is removed on the first aqueous extraction treatment, the extraction of the waste stems could probably be facilitated by mechanically extracting, draining and compressing. The stems would be discarded so that the resulting damage is unimportant.

Conclusions to Overall Extraction Work Performed

1. The freon 11-ammonia extraction system affords a method for removing 80-85% of the nicotine originally in the leaf material and 40-45% of the nicotine in stems. By this technique only one extraction is needed to obtain this efficiency. The expensive freon (solvent) would require recovery, possibly in a puffing type technique. With no other processing than air drying the tobacco is unsuitable as a smoking material.

2. When the extraction with freon is performed in a two-stage process the first extract might provide a source of natural flavor materials. The second extract would provide nicotine of higher purity than the one stage technique.

3. The water extraction technique is an efficient method for the removal of 80-85% of nicotine from leaf material or stems. The tobacco requires sequential extraction to obtain this efficiency. Partial reduction of the leaf nicotine (40-45%) may be obtained after one extraction.

CONFIDENTIAL

Whole leaf material can be processed with a burley drier and affords a smoking material comparable to the unextracted tobacco.

4. The aqueous extracts are dilute solutions of nicotine containing other dissolved or suspended materials. These solutions might be processed by high pressure technology currently unavailable for laboratory evaluation, or by liquid-liquid extraction.
5. The advantages of the water compared to the freon extraction include less physical and organoleptic damage to the tobacco. Conversely, the freon method lends itself to an easier and more straightforward workup of the extracted material and the extracts.

Recommendations from Overall Extraction Work

1. Specific projects should be initiated in cooperation with engineering personnel with a view to evaluating the applicability of pilot plant scale high pressure distillation processes.
2. Investigation into extraction processes and the availability of outside technical consultants having expertise in the area of extraction, such as the French Oil Mill Machinery Company.

Source: https://www.industrydocuments.ucsf.edu/docs/lpcg0054

CONFIDENTIAL

Appendix

Distribution Coefficients of Nicotine Between Water and Organic Solvents[12]

$K = C/C'$ where C represents the concentration of nicotine in the aqueous phase and C', the concentration of nicotine in the organic phase, both in grams per liter

Solvent	Distribution Coefficient, C/C', at		
	10°C	25°C	40°C
Chloroform	0.016	0.013	0.008
Ethylene dichloride	0.104	0.068	0.057
Undecanol	0.154	0.082	0.062
Chlorobenzene	0.147	0.083	0.053
α-Dichlorobenzene	0.159	0.093	0.057
Benzene	0.187	0.104	0.075
Carbon tetrachloride	0.193	0.116	0.074
Nitrobenzene	0.223	0.124	0.117
Toluene	0.243	0.137	0.079
1,4-Dichlorobutane	0.208	0.142	0.642
p-Cymene	0.214	0.148	0.133
Butyl acetate	0.382	0.166	0.121
Xylene, A.C.S.	0.338	0.181	0.234
Dichloroethyl ether	0.251	0.181	0.689
sym-Tetrachloroethylene	...	0.181	0.107
Cyclohexane	1.160	0.557	0.268
n-Heptane	...	0.942	0.526
Kerosene	...	1.11	...
Deobase	2.84	1.25	0.63

CONFIDENTIAL

References

1. Lorillard Memorandum, J. Reid to Dr. H. J. Minnemeyer, Dec. 10, 1976. Subject: Waste Tobacco.
2. Ward, G. M., Nicotine - A Product of Tobacco, Technical Bulletin 38, Dominion of Canada, Dept. of Agriculture (1941)
3. Skibbe, A., Water Extracts from Tobacco, Dept. of Agriculture, First Triennial Conference 474-84 (1928)
4. Ray, M., Rev. intern. tobacs 23, 132 (1948) C.A. 43:8617a (1949)
5. M. Brinkmann, K.G., Ger. 957,019, Jan 24, (1957), C.A. 53:10676d (1959)
6. Strolle, E.O., Claffey, J.B., Beinhart, E.G., Cane Milling of Nicotine from Green Nicotiana Rustica, USDA Bulletin, ARS-73-59, Feb. (1969)
7. Moser, Glenn P., U.S. Pat. 3,151,118, Sept. 29 (1964) to R. J. Reynolds Tobacco Co. CA 61:16459e (1964)
8. Fritzsche, Reinheld, Syracuse Chemist 35, No. 7, 3 (1942) C.A. 36:3909^{6} (1942)
9. von Bethmann, Max Freiherr; Lipp, Gerhard and Bayer, Helmut, U.S. Pat. 3,396,735 Aug. 15, 1968
10. Council of Sci. and Indian Research Indian 45,666 (1953)
11. Naude, C. P., Union South Africa Dept. of Agriculture Science Bulletin 278, 128 (1947)
12. Badgett, C. O., Ind. Eng. Chem. 42 2530 (1950)
13. Hind, J., U.S. Pat. 3,046,997 (1962) to Philip Morris Incorporated
14. Jones, S., Ger. Offen. 2,105,446 (1971) to R. J. Reynolds Tobacco Company
15. Staley, John and Clarke, Allen Bellerby U.S. Pat. 3,139,435 June 30 (1964) to Philip Morris Incorporated
16. Jackson, Kirby E. Alkaloids of Tobacco, Chem. Rev. 29, 123, (1941)
17. Bevard, F. C., Swiss 272,829, Jan. 15 (195) to Bevard & Cie
18. Hyatt, R., U.S. Pat. 2,117,558 (1938) to R. J. Reynolds