

Toxic and fine particulate emissions from U.S. refinery coking and cracking of 'tar sands' oils

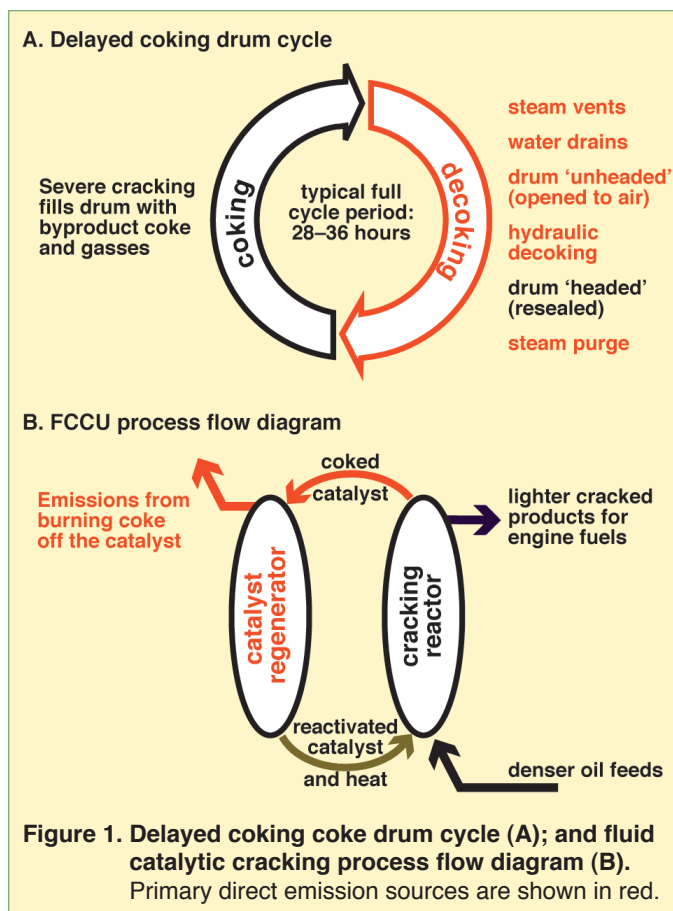
Greg Karras (2015).*

Emissions of toxic and criteria air pollutants from delayed coking units (DCUs) and catalytic cracking units (CCUs) were assessed for scenarios in which 20–50% of current US refinery crude oil feed might be replaced by diluted bitumen (dilbit) oils. Refinery- and process-level data for feedstock properties, process capabilities, and emissions were compared across the US industry to estimate changes in processing needed to maintain transport fuels production from the changing feedstock, and in resultant emissions. The shift from mid-barrel to denser and more contaminated oils from crude distillation of dilbits could swing hydrocracking to diesel and jet fuel and would increase DCU and CCU feed rates and coke yields. Volatile emissions from DCUs could increase by 14–47% and coke combustion emissions from CCUs could increase by 14–25% in +20–50% dilbit scenarios. Condensable particulate matter emissions from CCUs could increase by 500–1,300 metric tons per year (t/y) in the +20% dilbit scenario and 900–2,400 t/y in the +50% dilbit scenario. Benzene emissions from DCUs, though poorly measured, might increase by 46–95 t/y, and 150–320 t/y, in the respective scenarios. These industry-wide estimates for US DCUs and CCUs assume a plausible but elective crude oil switch without mitigation, and are limited by a paucity of measurements for most of the >100 toxic chemicals found in emissions from these units. Future work might focus on feedstock-driven changes in storage tank, hydroprocessing, and coker byproduct emissions.

Introduction

US refineries have gradually shifted to denser, more contaminated, lower quality crude feeds over three decades¹ and have begun to exploit vast potential supplies of still denser and more contaminated heavy oil and bitumen.^{2,3} Bitumen—'tar sands' oil—is fundamentally different from conventional crude.³ Processing lower quality oil is known to increase oil refining pollution intensity by increasing the pass-through of toxic elements in the oils,⁴ the fuel combustion for energy needed to refine them^{5–10} and the frequency and magnitude of plant upsets, spills, fires and flaring.^{11–13} However, relatively little has been done to characterize feedstock-driven emissions from some high-emitting refinery processes—including the delayed coking and catalytic cracking processes.

Delayed coking units (DCUs) account for ~95% of U.S. refining capacity to thermally crack residuum (resid),¹⁴ the densest and most contaminated fraction (cut) of crude from atmospheric or vacuum distillation. DCUs perform



severe thermal cracking at ~415–515 °C and ~15–90 psi for hours to yield liquid oils and contaminated byproducts that are typically burned as fuels, including hydrocarbon gasses, and petroleum coke that can be 9–12% volatile chemicals.^{15–18} This is a batch process that must interrupt feed to each reactor vessel (drum) to remove the coke, so DCUs typically have 2–8 drums in order to process resid semicontinuously. Decoking involves venting the drum, draining quench water from it, opening it to drill out the coke, and purging the drum after it is resealed—and all of that can introduce volatile chemicals to the atmosphere. *See* Figure 1. Direct measurements suggest that this inherently polluting design may place DCUs among the largest sources of volatile organic compounds such as benzene in refineries.¹⁹

Catalytic cracking units (CCUs) account for ~83% of US refinery capacity to crack heavy gas oil (HGO).¹⁴ HGO distills at ~343–566 °C and is the second densest, second most contaminated cut of whole crude after resid.

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Famously developed and deployed to convert HGO into high-octane gasoline, the process also can run resid,^{15–17} cycling the resid back into the reactor along with fresh feed, and many CCUs use this ‘recycle’ capacity.^{14, 20} Cracking occurs at $\approx 480\text{--}540^\circ\text{C}$ and $\approx 10\text{--}20$ psi in the presence of a catalyst to yield naphtha (gasoline feedstock), distillates (diesel and jet fuel feedstock), and byproduct gasses and coke.^{15–17, 21} The process is continuous. High-boiling hydrocarbons condense to deposit coke on the catalyst continuously, the catalyst cycles between the reactor and a ‘regenerator’ that reactivates the catalyst by burning the coke off of it continuously, and coke burn-off also heats the process. *See* Figure 1. Coke is high-emitting fuel. CCU ‘catalyst’ coke accounts for $\approx 99\%$ of coke burned in US refineries.²² CCUs are among the highest emitting refinery sources of combustion products such as condensable particulate matter (cPM).^{23, 24}

Bitumen is tar like or semi-solid petroleum that requires $\approx 2\text{--}3$ times more energy to extract, and to refine for engine fuels, than conventional crude, making it inherently high-emitting oil.^{5–10} Too viscous to transport by itself, bitumen is mixed with diluent oils such as naphtha in commercially exploited crude streams, and these diluent/bitumen blends are called dilbits. Distillation properties of dilbits differ markedly from those of the crude slate most US refineries were designed to process efficiently or process now. Figure 2 illustrates these differences. Dilbit distillation yield is low for HGO, especially low for mid-barrel distillates, and especially high for resid compared with the current average US crude slate and the Strategic Petroleum Reserve (SPR). Dilbit HGO

and resid cuts also are very dense (low API) and high in sulfur. Distillates are diesel and jet fuel feedstocks, while resid is fed to DCUs and CCUs to produce additional HGO that is added to CCU and hydrocracker feeds to produce distillate as well as naphtha. In other words, refining these high-resid, low-distillate oils means more DCU and CCU feedstock and more need for DCU and CCU products.

Process controls that are added onto the basic process design can capture or avoid a substantial part of process emissions, but technically feasible controls might not be deployed comprehensively, effectively, or at all, and in any case can control only a percentage of emissions generated by an inherently polluting design.^{18–20, 24–26} At any given level of such add-on controls, emissions are ultimately a function of process air pollutant generation. An example is increasing coke burn rate with increasing CCU feed rate, illustrated by data from a California plant in Figure 3: federal limits on PM emitted *per ton* coke burned in this CCU would not address its emissions from burning tons *per day* more coke. By increasing total DCU decoking cycle throughput, increasing CCU coke generation and burn-off, or both, changes in process feedstock associated with refining more dilbit would have the potential to increase emissions.

The work reported here compares publicly reported oil quality, processing, and emissions data to estimate refining sector-level changes in DCU and CCU processing, and emissions of toxic air pollutants and cPM, that could result from adding more dilbit oils to the US crude slate.

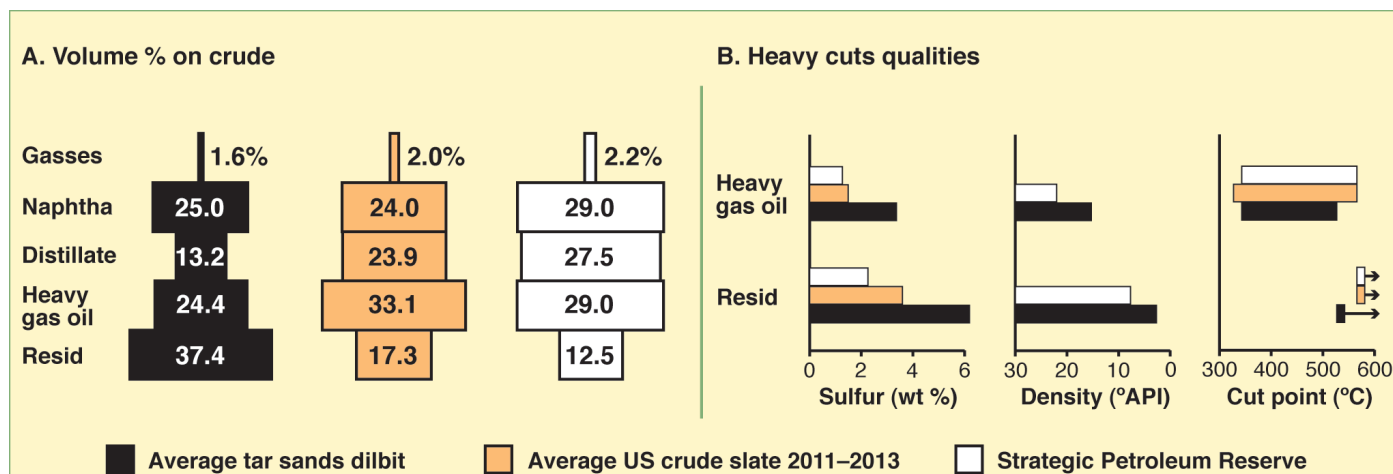
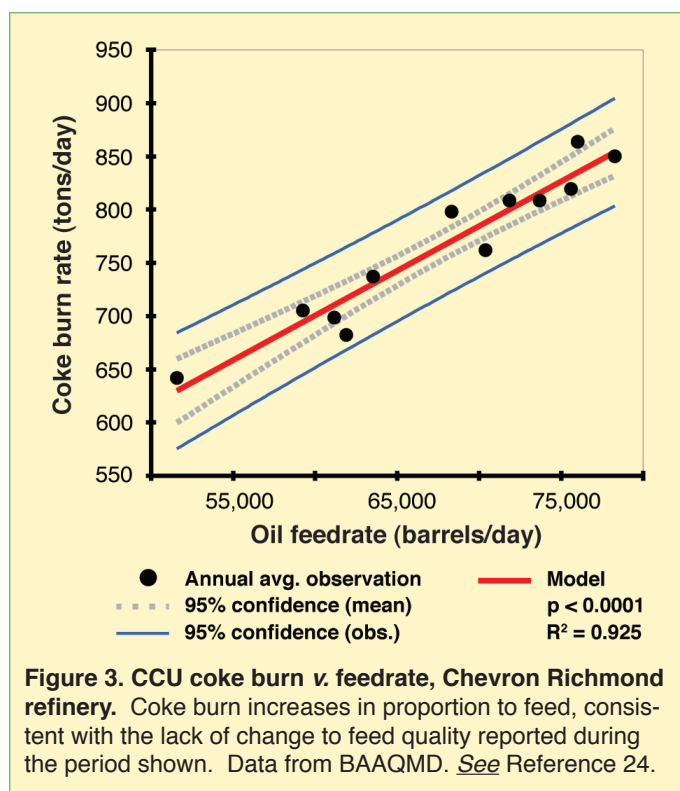


Figure 2. Distillation properties of dilbit, the current US refinery crude slate, and the US Strategic Petroleum Reserve. Data from Crudemonitor (2014); The ICCT (2013); and DOE (2002). *See* Supplemental Information, tables S1 and S2 for details. Heavy cut densities were not reported by The ICCT (2013) and were not available for the US Crude slate.

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Data and methods

Feedstock data for diluted bitumen (dilbit) oils and for the current average US refinery crude blend (slate) during 2011–2013 were reported by the oil industry, the International Council on Clean Transportation (ICCT), and the US Geological Survey, Department of Energy, and Energy Information Administration (EIA).^{1, 3, 27–33} (Data summarized here are provided, along with methods details, in the Supplemental Information (SI).)

Crude density, sulfur content, and distillation properties varied little among dilbits,²⁷ reflecting the intentional blending of these oils, and supporting the calculation of the ‘average’ dilbit shown in Figure 2. Properties of the current average US refinery crude slate were based on whole crude volume, density and sulfur content in 2013 reported by the EIA^{1, 30} and distillation yields estimated for 2011 by The ICCT.²⁸ EIA did not report distillation yield for the US crude slate, but did report US refinery operating data that supported the ICCT estimate. These values for 2013 reported by EIA were within 0.2%, 2.2%, 0.0%, and 1.2% of the ICCT estimate for whole crude density, whole crude sulfur content, HGO distillation yield processed in downstream units, and resid yield processed downstream, respectively. (SI Table S2.)

Potential changes in distillation yields were calculated as weighted averages for barrel-for-barrel replacement of the current average US crude slate with 20%, and 50%,

more of the average dilbit. Results confirmed the potential for changes in the volume, density, and sulfur content of distillate, HGO, and resid yields from crude distillation that are suggested in Figure 2. *See* Table 1.

Processing data for the conversion of resid and HGO into feedstocks for gasoline, diesel and jet fuel finishing (naphtha and distillate) were reported by the EIA and the petroleum engineering literature.^{15–17, 21, 31–34} Observed process capacities and oil feed rates confirmed the dominance of DCUs and CCUs among US refinery conversion (cracking) processes, and also the significant role played by hydrocracking units (HCUs).^{31, 33, 34} HCU capacity to crack gas oil was 1.297 million barrels/day (MMb/d), or 64% of total US HCU capacity, in 2014. (SI Table S4.) The HCU process differs from those of DCUs and CCUs in its use of hydrogen addition rather than carbon subtraction chemistry to accomplish cracking,^{15–17} and in its ability to ‘swing’ between naphtha (gasoline) and distillate (diesel and jet fuel) production targets.²¹ That ability would be important in addressing the loss of distillate from crude distillation of dilbits revealed in Table 1. For these reasons, gas oil HCUs were included in the analysis of conversion process changes that could result from adding more dilbit to the US crude slate.

Comparisons of +20–50% dilbit scenario distillation yields with current process capacities and rates revealed limited capacity to convert the additional resid into lighter feedstocks unless CCUs processed some of this resid or new coking capacity was built. (SI tables S3–S7.) While both solutions are technically feasible and each likely would be used in some cases, it was judged more likely overall that existing capacity would generally be used first before adding new capacity. Thus processing of resid in both DCUs and CCUs, with feed recycling to improve conversion in CCUs, was analyzed for these scenarios. Greater densities and sulfur contents of unit feeds containing more dilbit-derived resid is one important implication for processing in these scenarios.

Process design and operating data showed that, while product yields vary with unit design and operating details, when other factors were optimized, denser and higher sulfur feeds reduce liquid yields and increase coke yields from DCUs and CCUs. (SI Table S5.) Conversion process yield data that were found to best represent current and +20–50% dilbit scenario average process capacities and feeds are summarized in Table 2.

The DCU yields shown in Table 2 for 8.2 °API, 3.4% sulfur feed were applied to both the current slate and the +20–50% dilbit slates. However, dilbit-derived resid (Figure 2) is denser than 8.2 °API and exceeds 3.4% sul-

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Table 1. Potential changes in distillation yields from 20–50% more dilbit in the US crude slate.

		Current (2011-13)	20/80 dilbit/current scenario		50/50 dilbit/current scenario	
		Crude slate	Crude slate	Change (Δ)	Crude slate	Change (Δ)
Crude						
Volume	(MMb/d)	15.312	15.312	None	15.312	None
Density	(kg/m³)	872	883	Denser	899	Denser
Sulfur	(wt. %)	1.4%	1.9%	More sulfur	2.6%	More sulfur
Yield volumes						
Gasses	(MMb/d)	0.306	0.295	−0.011	0.279	−0.027
Naphtha	(MMb/d)	3.675	3.707	0.032	3.754	0.079
Distillate	(MMb/d)	3.660	3.332	−0.328	2.840	−0.820
HGO	(MMb/d)	5.068	4.801	−0.267	4.399	−0.669
Resid	(MMb/d)	2.649	3.264	0.615	4.188	1.539

Data from references 1 and 27–33. *See* SI Table S3 for details.

fur. If actual DCU yield in the dilbit scenarios is closer to that shown in Table 2 for the 4°API, 5.3% sulfur feed, this analysis might underestimate DCU and CCU feed rate increments in those scenarios. Similarly, although CCU yield data for the lighter feed shown in Table 2 was applied in the current baseline while that for the denser, 15.1 °API (3.3 % sulfur) feed was applied in the dilbit scenarios, CCUs would feed denser, higher sulfur resid derived from dilbit in those scenarios. If actual yields in the dilbit scenarios are lower than this 15.1 °API, 3.3% sulfur feed data estimate for light liquids, or if they are higher for coke, or both, this might underestimate CCU feed rate increments and coke-burn emissions in those scenarios. The use of these process yields for dilbits thus represents a conservative assumption.

These process yield data were applied to the crude distillation volume changes shown in Table 1 to estimate the changes in DCU, CCU, and gas oil HCU process feeds and rates that would be needed to maintain naphtha and distillate production in the +20–50% dilbit scenarios. The estimates were further constrained by an additional

objective to use existing DCU and CCU capacity before adding conversion capacity. As stated, this approach used existing CCU capacity for resid as well as HGO feed. Gas oil HCU ‘swing’ capacity was used to balance naphtha and distillate production so that both fuel feedstocks were maintained at current production volume. Other approaches are feasible but the cost of new capacity and value of motor fuel products was judged to support this approach. A check on this approach showed that, without changing CCU feeds, substantially more coking capacity was needed to approach current product yields even in the +20% dilbit scenario (*SI Table S7*), and growing or stable US refinery production rates with growing exports of these key products (*SI Table S8*) also supported this approach. Various changes in equipment (e.g., pumps, distillation internals) and product shifts among plants would be needed in any case.

Emissions were estimated relative to current conditions in percent, and as mass-rates for selected pollutants. The incremental emissions from DCUs were based on the volume of volatile material processed in the coke drums

Table 2. Representative conversion process yields by unit feed quality or product target.

		Delayed coking ^a		Catalytic cracking ^b		Gas oil hydrocracking ^c	
Product target		—	—	—	—	naphtha	distillate
Feed quality							
density	(°API)	8.2	4.0	20.1	15.1	22	22
sulfur	(wt. %)	3.4	5.3	0.5	3.3	2.5	2.5
Process yields							
naphtha	(vol. %)	19	24	58	51	90	29
distillate	(vol. %)	—	—	18	21	—	69
HGO	(vol. %)	45	30	—	—	—	—
coke	(wt. %)	25	35	7.0	10.3	—	—

(a) Data from reference 15. (b) Data from reference 17. (c) Data from reference 21. *See* SI Table S5 for details.

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and thus exposed to the atmosphere during decoking. This was estimated as the increase in DCU feed volume rate for each dilbit scenario by the analysis of process changes described above. Incremental emissions from CCUs were based on the mass of coke burned in CCUs. This was estimated from the increments for CCU coke yield (wt. %), feed vol./day, and feed density (current HGO $\approx 922 \text{ kg/m}^3$; dilbit resid $\approx 1,055 \text{ kg/m}^3$) found by the analysis of process changes. (*SI Table S6.*)

Mass emission rates were estimated by applying these relative increments to available measurements of specific pollutants in current ‘baseline’ DCU and CCU emissions.

Direct measurements of emissions were reported by Chambers et al.,¹⁹ US EPA,²⁰ the Bay Area Air Quality Management District,^{35,36} and Sánchez de la Campa et al.³⁷ Some 114 toxic chemicals were found in emissions from DCUs, CCUs, or both.²⁰ (*SI Table S9.*) But only a handful of these pollutants were measured above method detection levels (MDLs) consistently at multiple plants.²⁰

DCU source tests for a 2011 Information Collection Request (ICR) used sampling methods for other sources that often collected too little sample for analysis.²⁰ Source tests were reported for 5 DCUs. Multiple tests were below MDLs in all runs for nearly every analyte except VOC, methane, and benzene (measured in 5, 5, and 4 of the tests, respectively). Emissions/barrel DCU feed reported for VOC, methane and benzene ranged by more than two orders of magnitude, but only DCU vents—not coke drilling or other decoking steps—were measured.²⁰

Direct measurements of DCU decoking emissions by differential absorption light detection and ranging (DIAL)¹⁹ found VOC and benzene emissions that exceeded the ICR vent emissions maxima by 1–2 orders of magnitude. (*SI Table S12.*) These DIAL measurements were validated and close to the median results from 16 other refineries.¹⁹ Based on these data, vent tests alone may understate DCU emissions substantially. The DIAL data were judged more representative of DCU emissions, but only one unit was measured and \approx half of its emissions were from coke water handling. DIAL data were scaled to the minimum decoking frequency for DCUs and minimum decoking emission period measured, and coke water emissions were removed from the lower bound values, in the estimate derived from these data. (*SI tables S11, S12.*) This estimate, shown in Table 3, was judged to be the most conservative available based on the limited data from direct measurements of total decoking emissions. A check against benzene emissions in the Toxic Chemical Release Inventory (TRI) that were self-reported by refiners (*SI Table S15*) found that this estimate accounted for

Table 3. Delayed coker emission rates estimate.

Emissions per barrel (b) of coker feed

	Lower bound	Upper bound
Benzene (mg/b)	390	810
Methane (grams/b)	38	78
C ₂₊ VOC (grams/b)	63	130

Upper bound estimates include emissions from coke water handling. Data from reference 19 and SI tables S11, S12.

60% of total TRI benzene emissions from US refineries at the lower bound and 125% of them at the upper bound, suggesting DCUs are a strong source, and that either TRI emissions are underestimated, or that US refiners handle coke water differently from the refinery tested by DIAL.

Source tests of 11 refiners’ CCUs were reported.^{20,35,36} Emissions were measured above MDLs in one or more test runs at 10 of these CCUs for cPM, 6–8 CCUs for various metals, and 8 CCUs for hydrogen cyanide (HCN). (*SI Table S14.*) Data distributions suggested that median values may better represent the central tendency of the emissions data than arithmetic averages. (*Id.*) However, correlations among pollutants and operating parameters that were consistent with cPM-boosting effects of ammonia injection, together with the potential that the small data set may under-represent high emitting units, supported 90th Percentile values as an upper bound on emissions estimated from these data. (*Id.*) A check against self-reported TRI emissions (*SI Table S15*) supported this estimate for metals but suggested the possibility that the source tests might not accurately represent average CCU emissions of HCN. Other data show that CCUs are strong emission sources of various pollutants including cPM and metals.^{23,37} Table 4 shows the CCU ‘baseline’ emission rates estimate for cPM and metals.

Table 4. Catalytic cracking unit (CCU) current ‘baseline’ emission rates estimate.

Emissions per barrel (b) of CCU feed

	Lower bound	Upper bound
Fine particulate (g/b)	2.04	5.28
Chromium ($\mu\text{g/b}$)	158	243
Lead ($\mu\text{g/b}$)	130	284
Manganese ($\mu\text{g/b}$)	275	580
Nickel ($\mu\text{g/b}$)	481	3,630
Mercury ($\mu\text{g/b}$)	22.8	66.1

Lower bound: median value; upper bound: 90th Percentile. Data from references 20, 35, 36 and SI Table S14.

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Results

US refining sector-level conversion processing changes needed to maintain naphtha and distillate production in the +20–50% dilbit scenarios are shown in Table 5.

Generally, Table 5 shows changes in oil feed flows and process rates for conversion of the additional resid from distillation of the crude slates containing more dilbit into enough gas oil and distillate to maintain gasoline, diesel, and jet fuel production despite the shortfalls in GO and distillate from crude distillation of the dilbit. Incremental changes from current ‘baseline’ are shown.

In the +20% dilbit (20/80 dilbit/current slate) scenario, coking rate increases to 98% of capacity, producing 0.065 million barrels/d (MMb/d) of additional naphtha and 0.153 MMb/d of gas oil—not enough GO to erase the deficit from crude distillation, but resid feed to CCUs increases more than GO feed drops. Recycling this new resid feed the equivalent of 0.86 times boosts the CCU recycle rate by 0.235 MMb/d, or 5.5 vol. % of total CCU fresh feed. Together with the overall increase in fresh feed (0.161 MMb/d), the net CCU feed rate increment is 0.396 MMb/d. Assuming the CCU yield on this increment for 15.1 °API, 3.3 % sulfur feed in Table 2, these coking and CCU changes boost naphtha to 0.299 MMb/d above baseline while distillate remains 0.245 MMb/d below baseline, allowing HCU to swing from naphtha to distillate production and make up those differences. This swings 0.355 MMb/d or 27% of GO HCU capacity from naphtha to distillate production.

Net changes in processing for this 20/80 dilbit/current crude slate scenario boost coking and CCU feed rates by an estimated 0.340 and 0.396 MMb/d, respectively, but both processes remain within their nominal capacities while those rate increments achieve essentially zero net change in gasoline, diesel, and jet fuel feedstock.

In the +50% dilbit (50/50 dilbit/current slate) scenario, processing changes follow the same pattern but are larger with coking and CCU feed rates increasing by 1.138 and 0.723 MMb/d, respectively, and achieve similar net-zero changes in naphtha and distillate production, but at a coking rate that exceeds current capacity.

Total utilization of 2014 coking capacity is 128% for the 50/50 dilbit/current crude slate scenario in Table 5. This suggests that new conversion capacity would be built in the +50% dilbit scenario. That finding is consistent with refinery engineering knowledge—and, in fact, the coking capacity of US refineries has doubled since 1987.³⁴

Results indicating < 100% utilization of capacity should be interpreted in the context of the capacity ‘optimiza-

tion’ approach discussed in the methods section. New capacity could be built for various reasons, and if built, could be used at rates greater than those conservatively estimated in Table 5. For example, plants that lack DCU, CCU, or HCU capacity may build it instead of transferring intermediate products to other plants that have these capacities. Also, lower yields from boosting CCU recycle rates may force new capacity for the increased fresh feed rates needed to meet product targets. In any case, the differences in distillation properties from a switch to 20–50% more dilbit in the crude slate could require changes to pumps, exchangers, distillation unit internal configurations and piping, and other refinery equipment.

CCU coke yield increments estimated in Table 5 reflect increased feed rate *and* the increase in coke burn rate per barrel of CCU feed that would be driven by the lower quality of the new dilbit resid feed increments processed in CCUs. These increments represent a coke burn rate of ≈ 17.3 kg/b, based on the coke yield of 10.3 wt. % in Table 2 and the average density of the dilbit resid (1,055 kg/m³; *SI Table S1*). This compares with ≈ 10.3 kg/b for current ‘baseline’ coke yield (7 wt. %) and HGO feed (≈ 922 kg/m³; *SI Table S2*). Thus, the dilbit scenarios would result in burning $\approx 68\%$ more catalyst coke per barrel for the new feed processed by CCUs. Emissions per barrel of the new CCU resid feed would be greater than baseline emissions per barrel by this amount, on average. Emission per barrel estimates applied to the new CCU resid feed increments are shown in Table 6.

Results for emission increments in the dilbit scenarios are summarized in Table 7. Volatile pollutant emissions from decoking operations exposing larger throughputs to the atmosphere at DCUs in US refineries could increase by $\approx 14\%$ in the +20% dilbit scenario and by $\approx 47\%$ in the +50% dilbit scenario. This estimate is based on the 0.340–1.138 MMb/d increments over the 2.303 MMb/d current feed rate shown in Table 5, conservatively scaled downward to the portion of total coking capacity represented by DCUs (94.6%). Estimated average benzene and volatile organic compound (VOC) emission increments for US refinery DCUs are based on these scaled increments applied to the DCU emission-per-barrel rates in Table 3. Benzene emissions from the DCUs could increase by an estimated 46–95 metric tons per year (t/yr) in the +20% dilbit scenario and by 150–320 t/yr in the +50% dilbit scenario. VOC emissions from the DCUs could increase by an estimated 7,400–15,300 t/yr in the +20% dilbit scenario and by 24,700–51,100 t/yr in the +50% dilbit scenario. These pollutant-specific DCU increments are based on a conservative interpretation of

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Table 5. Estimated changes in conversion processing to maintain US gasoline, diesel and jet fuel production in scenarios with 20–50% more dilbit entering the current US crude slate.

Values in millions of barrels per day (MMb/d) or as noted

	20/80 dilbit/current scenario	50/50 dilbit/current scenario
Change in crude dist. unit (CDU) yield		
Naphtha, change from crude distillation	0.032	0.079
Distillate, change from crude distillation	–0.328	–0.820
Gas oil, change from crude distillation	–0.267	–0.669
Resid, change from crude distillation	0.615	1.538
Changes in coking rate and yield		
Net change in coking feed rate	0.340	1.138
Change in coker naphtha yield	0.065	0.216
Change in coker gas oil (GO) yield	0.153	0.512
Change in GO from CDU + coking	–0.114	–0.157
Change in resid from CDU + coking	0.275	0.400
Changes in CCU rate and yield		
Change in CCU fresh feed input	0.161	0.243
Change in CCU recycle rate	0.235	0.480
New resid feed % of total CCU fresh feed	5.5%	7.9%
Equivalent times new resid feed is recycled	0.86	1.20
Net change in CCU total feed rate	0.396	0.723
Change in CCU naphtha yield	0.202	0.369
Change in CCU distillate yield	0.083	0.152
Change in CCU coke yield (MM kg/day)	6.84	12.5
Change in CDU+coking+CCU naphtha	0.299	0.664
Change, CDU+coking+CCU distillate	–0.245	–0.668
Changes in GO-HCU rate and yield		
Net change in HCU GO feed input	0.000	0.000
Δ in GO-HCU feed input for naphtha	–0.355	–0.970
Δ in GO-HCU feed input for distillate	0.355	0.970
Change in GO HCU naphtha yield	–0.216	–0.592
Change in GO HCU distillate yield	0.245	0.669
Net changes in processing and key yields		
Coking capacity in 2014 (MMb/cd)	2.687	2.687
Coking feed rate in 2013 (MMb/d)	2.303	2.303
Net Δ in coking feed rate (MMb/d)	0.340	1.138
Total utilization of 2014 capacity (%)	98%	128%
CCU capacity in 2014 (MMb/cd)	5.616	5.616
CCU feed rate in 2013 (MMb/cd)	4.811	4.811
Net Δ in CCU feed rate (MMb/d)	0.396	0.723
Total utilization of 2014 capacity (%)	94%	98%
GO-HCU capacity, 2013 (MMb/cd)	1.297	1.297
GO-HCU feed swung to distillate (%)	27%	75%
Naphtha (gasoline feedstock)		
Net Δ from CDU, coking, CCU and HCU	0.082	0.072
Net Δ v. baseline CDU yield (%)	2%	2%
Distillate (diesel, jet fuel feedstock)		
Net Δ from CDU, coking, CCU and HCU	0.000	0.001
Net Δ v. baseline CDU yield (%)	0%	0%

Data from tables 1 and 2, except current process capacities and rates from refs. 31, 33, 34. [See](#) SI Table S1–S7 for details.

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Table 6. Catalytic cracking unit (CCU) potential emission rates estimate for dilbit oil increments.

Emissions per barrel (b) of CCU feed

		Lower bound	Upper bound
Fine particulate	(g/b)	3.43	8.89
Chromium	(µg/b)	266	409
Lead	(µg/b)	219	478
Manganese	(µg/b)	463	976
Nickel	(µg/b)	810	6,110
Mercury	(µg/b)	38.4	111

Based on data from Table 4, 10.3 wt. % coke yield for denser 1,055 kg/m³ resid feed; rates for resid feed increments only.

the limited available data from direct measurements of DCU emissions and are subject to the caveats regarding the available DCU data discussed in the methods section.

CCU emissions from US refineries could increase by an average of ≈ 14% in the +20% dilbit scenario and by an average of ≈ 25% in the +50% dilbit scenario. These increments are based on burning more coke in CCUs and are estimated based on the coke yields in Table 5 and that calculated from the baseline data cited above at the 4.811 MMb/d baseline feed rate in Table 5. (*SI Table S6.*)

Changes in CCU feed volume and coke yield account for ≈ 59% and 41% of these increments, respectively. (*Id.*) CCU emission increments for specific pollutants are based on the emission-per-barrel rates in Table 6 and the CCU dilbit scenario feed rate increments in Table 5.

Average US refinery CCU emissions of condensable particulate matter could increase by 500–1,300 t/yr in the +20% dilbit scenario and by 900–2,400 t/yr in the +50% dilbit scenario. For metals, these estimates suggest that average US refinery CCU emissions could increase, in the +20% and +50% scenarios, respectively, by 38–59 and 70–110 kg/yr for chromium, by 32–69 and 58–130 kg/yr for lead, by 67–140 and 120–260 kg/yr for manganese, by 120–880 and 210–1,600 kg/yr for nickel, and by 5.5–16 and 10–29 kg/yr for mercury.

Because they are based on changes in the processes generating volatile chemical emissions from DCUs and coke combustion product emissions from CCUs, the relative percent increments in Table 7 also apply to the (large) subsets of those pollutants that are not yet quantified well by direct measurements of these emissions. At least 114 toxic chemicals have been identified in DCU emissions, CCU emissions, or both. (*SI Table S9.*)

Discussion

This work confirms that replacing more of the current US refinery crude slate with ‘tar sands’ dilbit oil has the potential to increase emissions of air pollutants that have local and regional environmental health implications from delayed coking and catalytic cracking units. DCUs and CCUs would process denser and lower quality oils in greater amounts, boosting the amounts of volatile chemicals entering the air from decoking and the amounts of combustion products from burning more coke in CCUs.

Table 7. Potential increase in delayed coking and catalytic cracking unit emissions estimated for scenarios in which 20–50% of the baseline US crude slate is replaced by tar sands dilbit oil.

Increments in percent and mass rate

		20/80 dilbit/current scenario	50/50 dilbit/current scenario
Delayed Coking			
Emission increment	%	+ 14 %	+ 47 %
Benzene	tons/yr	46 — 95	150 — 320
Volatile organic carbon (C ₂₊)	tons/yr	7,400 — 15,300	24,700 — 51,100
Catalytic Cracking			
Emission increment	%	+ 14 %	+ 25 %
Particulates (condensable)	tons/yr	500 — 1,300	900 — 2,400
Chromium	kg/yr	38 — 59	70 — 110
Lead	kg/yr	32 — 69	58 — 130
Manganese	kg/yr	67 — 140	120 — 260
Nickel	kg/yr	120 — 880	210 — 1,600
Mercury	kg/yr	5.5 — 16	10 — 29

Total increments from these units at U.S. refineries—individual plant emissions will vary. DCU increments from greater decoking throughputs. CCU increments from greater coke-burn rates caused by increased feed rates and coke yields. *See SI for details.*

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Direct measurement data are limited, especially for DCUs, but available data suggest that these emission increments would be significant. Benzene increments estimated for the US fleet of DCUs are 9–18% of benzene emissions reported from all US refinery sources by the Toxic Chemical Release Inventory (*SI Table S15*) in the +20% dilbit scenario and 29–62% of that TRI estimate in the +50% dilbit scenario. Emission increments reported here are US averages—individual plant emissions will vary—but if these VOC and cPM increments were realized at a ‘notional’ refinery with a 50,000 b/d DCU and 80,000 b/d CCU (*SI Table S16*), the resultant emissions could exceed the environmental significance thresholds applied in the San Francisco Bay Area (10 short tons/yr) for both pollutants.

Future work should consider feedstock-driven emissions from other refinery sources. The diluents in dilbit could boost volatile ‘fugitive’ emissions from crude oil storage tanks in amounts that, DIAL measurements suggest,¹⁹ may be underestimated by traditional emission modeling. Substantial CO₂ emission from hydrogen production for the extra gas oil hydrocracking and hydrotreating needed to process bitumen has been documented,^{6–10} but flaring from gas oil hydroprocessing warrants more attention. This exothermic, high pressure, hard-to-control process²¹ can dump sulfur-rich gasses in amounts that overwhelm flare gas recovery systems when reactors depressure during upsets. Feedstock-driven expansion of gas oil hydroprocessing could thus increase the frequency and magnitude of flare emission incidents at refineries.

Emissions associated with DCU byproducts also warrant more attention. Most of the coke yield from DCUs is burned after it leaves the refinery gate,²² much of it is exported overseas (*SI Table S8*), and coke by-production rises predictably as denser, higher sulfur crude is processed (*SI Table S17*), but the resultant emissions often are ignored by refinery and fuel cycle assessments. The byproduct gasses that are collected before venting starts in the decoking part of the DCU drum cycle are burned as fuel gas throughout refineries, and these coker gasses contain sulfur compounds that are uniquely resistant to the amine scrubbing typically used by refinery fuel gas systems.²³ Emissions from increased by-production of this ‘dirtier’ fuel gas as cokers process more resid should be considered in assessments of refining dilbit oils.

Ultimately, there are alternatives to refining bitumen, and the most important uncertainty in estimates of future emissions from refining more of this ‘tar sands’ oil involves public policy choices among these alternatives.

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Supporting Information Available

Data and details of methods; 34 pages including references and 17 annotated tables.

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